JOURNAL OF CATALYSIS **106**, 251–262 (1987)

Nature of Active Species in the Ammoxidation of Toluene over V_2O_5/TiO_2 Catalysts Prepared by Flash-Drying

FABRIZIO CAVANI, ELISABETTA FORESTI, FERRUCCIO TRIFIRÒ,[1]
AND GUIDO BUSCA*

*Dipartimento Chimica Industriale Edei Materiali Viale Risorgimento 4, 40136 Bologna, Italy, and *Istituto di Chimica, Facoltà di Ingegneria, Viale Risorgimento, 40136 Bologna, Italy*

Received August 21, 1986; revised December 17, 1986

V/Ti/O catalysts were prepared by flash-drying of solutions containing V(IV) and Ti(IV) ions, thus with contemporaneous hydrolysis and precipitation of V_2O_5 and TiO_2, as anatase. The catalysts were characterized by means of X-ray diffraction, (XRD), chemical analyses, Fourier transform infrared spectrometry, (FTIR) and thermogravimetry. The results indicate that at least three different forms of vanadium are present in the calcined samples: (1) a V(IV) stabilized as regards oxidation, but reducible to V(III), which strongly interacts with the support, and probably constitutes the so-called monolayer spread over the anatase surface; this species is characterized by an IR absorption at 940 cm^{-1}; (2) a V(V) species, easily reducible to V(IV), and to V(III), characterized by an IR band at 980 cm^{-1}; this species also strongly interacts with the TiO_2; and (3) vanadia weakly interacting with the TiO_2, present as amorphous V_2O_5. Catalysts containing different amounts of vanadium were tested in the ammoxidation of toluene to benzonitrile, and in the dehydrogenation of isopropyl alcohol to acetone. The correlation between the amounts of the different vanadia species and the activities indicated that species 1 possesses the active sites responsible for toluene activation and alcohol dehydrogenation; species 2 instead is responsible for the parallel undesired combustion of ammonia to nitrogen; while the third species is inactive in all reactions. © 1987 Academic Press Inc.

INTRODUCTION

V/Ti/O catalysts have been widely studied and characterized for oxidation reactions of different organic substrates, such as aromatic hydrocarbons (especially *o*-xylene) (*1–6*) and olefins, and in the ammoxidation of some alkylaromatics, such as alkylpyridine, or xylenes (*7–12*).

These catalysts are usually prepared by the wet impregnation technique, thus by deposition of vanadium from a V(V) solution onto preformed TiO_2 (*13–15*). Other methods which have been used are the grafting technique (*16–17*), flame hydrolysis (*18*), and mixing of the two oxides followed by heating (*7, 8*).

A completely different preparation technique has been used in previous studies in order to prepare catalysts active and selective for the ammoxidation of aromatic compounds and oxidation of *o*-xylene to phthalic anhydride, by the contemporaneous precipitation of Ti and V oxohydrates (*10–12, 19*). The coprecipitation has been carried out by flash-drying, that is, by dropping a solution of titanium and vanadium (IV) ions on a hot ceramic plate at high temperature.

The aim of this research was to gain some insights on the nature of active sites in the ammoxidation of toluene to benzonitrile, and to compare the results and the model proposed with those for catalysts prepared by impregnation or grafting techniques.

In the case of catalysts prepared by impregnation or grafting methods it has been established that the surface structure

---

[1] To whom correspondence should be addressed.

0021-9517/87 $3.00

of these catalysts consists of a layer of vanadium oxide, spread onto the anatase surface, which contains the active sites for the formation of phthalic anhydride from *o*-xylene (*5, 6, 13–17, 20, 21*). This bidimensional structure is characterized by a different reactivity with respect to crystalline V_2O_5. The enhanced activity of vanadium has been explained by two different hypotheses. The first takes into consideration the presence of a crystallographic fit between the growth planes of anatase and the (010) planes of V_2O_5, the one containing the V=O bonds (*22*). This remarkable fit leads to the preferential exposure of the vanadyl centers, thus of the active sites (*13, 23*). The second hypothesis deals instead with the presence of a strong chemical interaction between the surface of anatase and the vanadium oxide. This interaction derives from the reaction of surface hydroxy groups of TiO_2 with vanadium, giving rise to the formation of a monolayer, where the V=O bond is characterized by a different bond strength and higher reactivity (*5, 14, 24, 25*).

In this work the model of a vanadium oxide monolayer on the surface of anatase as the active phase for ammoxidation also was checked in order to interpret the results obtained and the discrepancies found with the catalysts prepared with the impregnation method.

METHODS

Preparation of the Catalysts

The V(IV) solution was prepared by reducing V_2O_5 in an aqueous oxalic acid, at 70°C, until a deep blue solution was obtained. The Ti(IV) solution was obtained by dissolving $TiCl_4$ in a hydrochloric acid solution (pH less than 1), while keeping the temperature of the solution at 20°C. At this step hydrolysis of $TiCl_4$, with the formation of the blank precipitate, must be avoided. The two solutions were then mixed, in the relative amounts necessary to obtain the desired V_2O_5 content in the final catalyst. The quantitative precipitation was made by high-temperature hydrolysis, achieved by dropping the solution on a hot ceramic plate (temperature higher than 100°C), or on pellets of α-Al_2O_3, kept under mechanical stirring. In the latter case, the catalysts were used in that shape for the catalytic tests of toluene ammoxidation. This procedure led to the anatase structure for TiO_2; after the calcination treatment at 400°C the samples had a surface area of about 50 m^2/g.

Characterization of the Catalysts

Chemical analyses. The following procedure was adopted for the chemical analyses of the samples: (i) The calcined samples (T = 400°C) were treated with a NH_4OH/H_2O solution (pH about 11). This treatment leads to the dissolution of the vanadium oxide which does not interact chemically with the support (*13–15, 26*). Two fractions were so obtained: the solution containing the soluble vanadium oxide, subsequently acidified with H_2SO_4 until attainment of pH about 1, and the solid, constituted by the insoluble TiO_2 and by the vanadium interacting chemically with it. This latter fraction was dissolved in concentrated hot H_2SO_4. Preliminary tests on a standard solution revealed that this treatment does not lead to any change in the valence state of vanadium, because in strongly acid solutions the V(IV) is stable, and V(V) is not reduced.

(ii) The two fractions were analyzed separately with the manganometric method (*27*). In particular, a part of each fraction was titrated with 0.1 N $KMnO_4$, to determine the amount of V(IV) in the solution; another part was titrated with a Fe^{2+} solution in order to determine the amount of V(V). The validity of these kinds of analyses is supported by both tests on standard solutions, and the exact correlation between the total amount of vanadium determined with this method and the amount used for the preparation. Moreover, this technique has been applied successfully in the analyses of both V/P/O catalysts (*27–29*), and of V/Ti/O catalysts (*15, 16, 19, 23, 30*).

Other characterizations. X-ray diffraction analyses were performed with a Phillips X-ray diffractometer, using Ni-filtered Cu$K\alpha$ radiation. Thermogravimetric tests were carried out with a Perkin–Elmer TGS 2 thermobalance; for the reduction tests, a flow of 2% H_2 in He was used (0.5 cm^3/s), at a temperature of 380°C. Before these tests were made, the samples were calcined in air at 400°C. Fourier transform IR (FTIR) spectrometers were used, all connected with conventional gas manipulation devices, evacuation ramps, and measurement cells.

Catalytic Tests

Catalytic tests were carried out using a fixed-bed conventional flow reactor at atmospheric pressure. The reactor was a stainless-steel tube (4 mm in diameter, 600 mm long) placed in a copper bar and externally heated by electric resistances.

The effluents, kept at 270°C to prevent condensation, were analyzed using two gas chromatographs on-line to the reactor. The first gas chromatograph analyzed the unconverted toluene or isopropyl alcohol, and the benzonitrile or acetone and propylene formed; traces of other by-products (benzene and benzaldehyde from toluene, diisopropyl ether and propane from isopropyl alcohol) were not taken into consideration. The column was a Silicon oil DC 550, supported on Chromosorb W 80-100; the oven temperature was programmed from 80 to 220°C (heating rate 16°/min). The uncondensable gases (O_2, N_2, CO, and CO_2) were analyzed by the second gas chromatograph, using a Carbosieve S column; the oven temperature was programmed from 20 to 240°C (heating rate 8°/min).

The active V/Ti/O phase was supported over cylindrical pellets of ceramic, with a central axial hole for the insertion of a thermocouple; the thickness of the active phase was 60 m (6% by weight). Forty pellets (i.d. 1.0 mm, o.d. 4.1 mm, ht 4.0 mm) were used for each series of catalytic tests.

The absence of significant phenomena of bypass of the reactants was verified using H_2O and N_2 as gas tracers. The pressure drop along the catalytic bed was, in all cases, lower than 0.20 kg/cm^2. The absence of homogeneous combustion of the reactants or of the products at high temperature was verified. The absence of significant interparticle transport effects was verified by varying the amount of the catalyst, at a constant W/F ratio.

The experimental conditions for the tests of toluene ammoxidation were toluene, ammonia, and oxygen partial pressures in the feedstock 0.0117, 0.075, and 0.135 atm, respectively; the remaining was helium; total flow rate was 1.40 cm^3/s.

The experimental conditions for the tests of isopropyl decomposition were temperature, 200°C; alcohol partial pressure 0.00425 atm; the remaining was helium; total flow rate was 3.39 cm^3/s. In this case the catalyst was used as a powder (volume 1 cm^3), which ranged in particle size from 0.125 to 0.250 mm.

RESULTS

X-Ray Analyses

As noted under Methods, the preparation method used leads to the anatase structure after calcination. No rutile, or only traces, was observed in the samples after calcination. A detailed analysis of the X-ray diffraction maxima of anatase shows that no shift of the lines took place, and therefore no modification of the cell parameters and volume occurred. This indicates that probably no solid solution of vanadium in the anatase lattice occurred.

The diffraction maxima of V_2O_5 are not present, therefore indicating that most of the vanadium is present as some sort of bidimensional structure, not detectable by X rays. Also in the case where the amount of extractable vanadia is relatively high

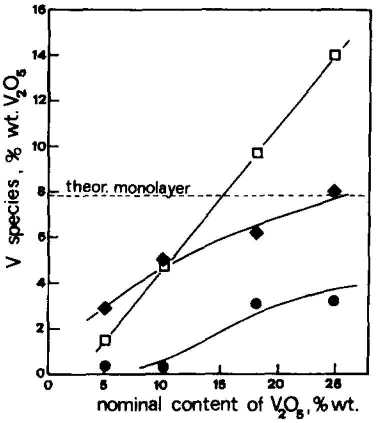

FIG. 1. Absolute amounts of the different vanadia species as functions of the nominal content of V_2O_5: (◆) insoluble V(IV); (□) insoluble V(V); (●) soluble V(V). Dashed line, theoretical monolayer.

(25% of V_2O_5 by wt), the diffraction maxima typical of V_2O_5 are not present. The X-ray spectrum of this catalyst, after extraction of the excess vanadia, is practically the same as the unwashed one, except for the disappearance of some background due to an amorphous phase. In addition, there are some weak lines (d = 4.13, 3.17, 2.90, 2.77, 2.55 Å) which are left by washing, that can not be attributed to any known TiO_2 phase, or to any vanadium oxide phase.

X-ray analyses of the sample calcined at 500°C shows the appearance of the diffraction maxima typical of crystalline V_2O_5. No X-ray lines of rutile were found after calcination at 500°C. Only after calcination at 600°C was 70% of anatase transformed to rutile, as determined on the basis of the X-ray analysis.

Chemical Analyses

Figure 1 shows the chemical analyses of samples containing different amounts of global vanadium after calcination at 400°C. It can be seen that generally three different kinds of vanadia species are detected: (a) a vanadia species which can be dissolved in a basic medium; this part, after calcination, is in the form of V(V); (b) two vanadia species which can be dissolved only in hot concentrated H_2SO_4, together with TiO_2; this part is present as both V(IV) and V(V). The chemical analyses of the 10% V_2O_5/TiO_2 sample calcined at 500°C is reported in Table 1. It is seen that an increase of the amount of soluble V(V) occurred, corresponding to a decrease of the surface area of the sample.

The chemical analyses of the catalysts after reaction (after stable catalytic behavior had been reached), and subsequently reoxidized at 400°C, are shown in Table 1. A comparison with the samples before reaction (Fig. 1) shows that in the 10% V_2O_5/TiO_2 sample, V(IV) increased up to an absolute amount similar to that of the 25% V_2O_5/TiO_2 sample. Also the amount of soluble vanadia increased and, correspondingly, the amount of V(V) which could not be dissolved decreased considerably. The surface area did not change during the reaction. The 25% V_2O_5/TiO_2 catalyst, after reaction and reoxidation, shows the same quantity of unoxidizable V(IV), an increased amount of soluble vanadia, and a corresponding decrease in insoluble V(V). Similarly to that observed for the 10% V_2O_5/TiO_2 catalyst, the 5% V_2O_5/TiO_2 sample after reaction was almost reduced to a V(IV) species which cannot be reoxidized.

Thermogravimetric Analyses

The 25 and 10% V_2O_5/TiO_2 samples were first oxidized at 400°C, and then reduced in a flow of 2% H_2 in He, at constant temperature (380°C). Shown in Fig. 2 are the differentiated weight loss curves as functions of the time of permanence of the samples in the reducing atmosphere. The total weight loss (reported in Table 1) for the 10 and 25% V_2O_5/TiO_2 samples corresponds to the theoretical weight loss for the total reduction of both insoluble and soluble V(V), and of V(IV) to V(III) (theoretical values 1.76 and 3.65%, respectively). The first weight loss, which occurs after a short

TABLE I

Chemical Analyses of the Spent and Subsequently Reoxidized Catalysts

V_2O_5 nom. content (% wt. V_2O_5)	Surface area (m^2/g)	Theoret. monolayer[a] (% wt. V_2O_5)	Soluble vanadium		Insoluble vanadium	
			V(IV)	V(V)	V(IV)	V(V)
			(% wt. V_2O_5)		(% wt. V_2O_5)	
5	57	8.4	(a) —	0.40	3.10	1.50
			(b) 0.25	0.70	3.80	0.25
			(c) —	0.95	3.80	0.25
10	52	7.6	(a) —	0.20	4.80	5.00
			(b) 0.60	1.40	7.30	0.70
			(c) —	2.00	7.30	0.70
10[b]	20	2.9	(a) —	2.10	3.90	4.00
			(b) 1.30	0.80	7.70	0.20
			(c) —	2.10	4.10	3.80
25	50	7.3	(a) —	3.00	8.00	14.00
			(b) 1.00	9.00	12.50	2.50
			(c) —	10.00	8.50	6.50

Note. (a) Catalyst calcined at 400°C. (b) Spent catalyst: the sample has been cooled in a nitrogen atmosphere. (c) Reoxidized catalyst (400°C, for 3 h).

[a] Ref. (*17*).

[b] Calcined at 500°C before catalytic tests.

time, corresponds to the reduction of the insoluble V(V) species to V(IV) (theoretical values 0.44 and 1.19% for the 10 and 25% V_2O_5/TiO_2 catalysts, respectively).

Infrared Characterization

The FTIR spectra of the samples (calcined at 400°C, washed with the ammonia solution, and calcined once again) are shown in Fig. 3, after subtraction of the contribution of TiO_2. They exhibit a main broad band in the range 940–980 cm^{-1}; the spectra of the unwashed samples are similar, except for the presence of a weak band at 1020 cm^{-1}, typical of the V=O stretching in crystalline V_2O_5. An intense band at 942 cm^{-1} is present in the 5% V_2O_5/TiO_2 sample. In the 25% V_2O_5/TiO_2 sample, the band seems to be centered around 975 cm^{-1}, even though the presence of a component around 950 cm^{-1} cannot be excluded. In the 10% V_2O_5/TiO_2 catalyst the band occurs at 950 cm^{-1}.

Ammoxidation of Toluene to Benzonitrile

Some samples (5, 10, and 25% V_2O_5/TiO_2) were tested in the reaction of toluene ammoxidation to benzonitrile, after calcination at 400°C. These catalysts show an initial inconsistent catalytic behavior for

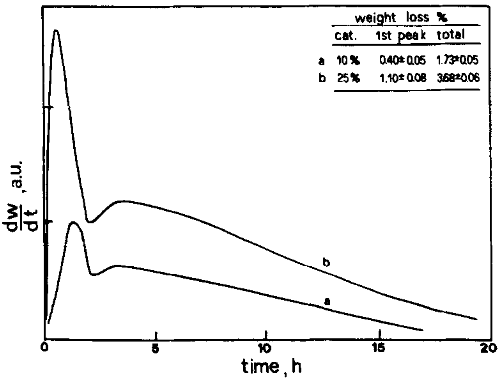

FIG. 2. Differentiated curves of isothermal weight loss; temperature 380°C; catalysts, 10 and 25% V_2O_5/TiO_2.

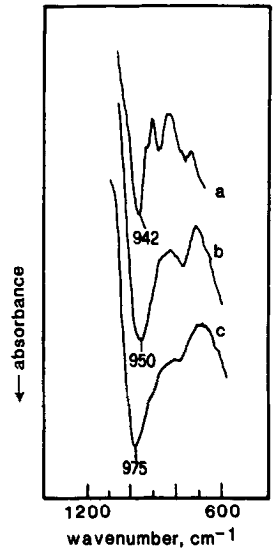

FIG. 3. Infrared spectra of the calcined 5% (a), 10% (b), and 25% (c) V_2O_5/TiO_2 catalysts.

the first hours of reaction. Shown in Fig. 4 are the maximum yield in benzonitrile and the yield in nitrogen at 320°C (from ammonia combustion) of the 25% V_2O_5/TiO_2 catalyst as functions of the time of permanence in the reaction medium at 380°C.

In particular, an increase in the maximum yield in benzonitrile is observed, along with a considerable decrease in the formation of nitrogen from the combustion of ammonia. Similar behavior was observed for the 10% V_2O_5/TiO_2 catalyst, except for a more enhanced increase in the maximum yield in benzonitrile from toluene ammoxidation (from 65 to 82%). After some hours, stable catalytic behavior is observed.

The catalytic behavior in steady-state conditions of the three samples is summarized in Fig. 5. In particular, this figure shows the productivities in benzonitrile and nitrogen at 320°C. Also shown is the behavior of the 10% V_2O_5/TiO_2 sample calcined at 500°C (instead of 400°C) before reaction. The activity of the catalyst calcined at the higher temperature is lower (and the maximum yield in benzonitrile also decreases). The combustion of ammonia to nitrogen is instead higher than in the case of the sample calcined at 400°C. Chemical analyses of the sample after reaction (Table 1) show that the sample is practically the same as before reaction (except for a higher average degree of reduction); subsequent reoxidation treatment however restores the original average degree of oxidation.

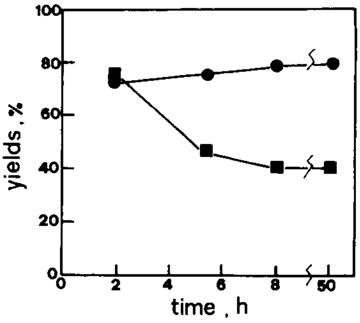

FIG. 4. Maximum benzonitrile yield (●) and nitrogen yield at 320°C (■) as functions of the reaction time; catalyst, 25% V_2O_5/TiO_2.

Tests of Isopropanol Dehydrogenation

Figure 6 shows the dependence of the concentrations of acetone and propylene

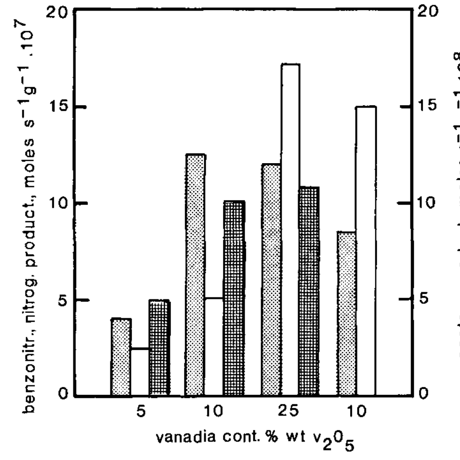

FIG. 5. Benzonitrile (▨), N_2 (□), and acetone (▦) productivities as functions vanadia content; catalysts, 5, 10, and 25% V_2O_5/TiO_2, and 10% V_2O_5/TiO_2 calcined at 500°C (●). Temperatures, 320°C (benzonitrile and nitrogen) and 200°C (acetone).

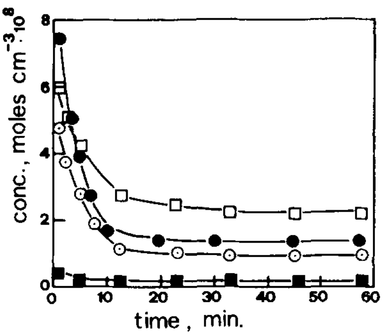

FIG. 6. Acetone (○, ●) and propylene (□, ■) concentrations at the outlet of the reactor as functions of the reaction time; catalyst, 10% V_2O_5/TiO_2 after calcination at 400°C (open symbols) and after ammoxidation of toluene (solid symbols).

formed on the decomposition of the isopropyl alcohol, as functions of the reaction time; traces of other products such as diisopropyl ether or propane are not shown. The catalyst is 10% V_2O_5/TiO_2 after calcination at 400°C and after it had been tested in the ammoxidation of toluene. It is shown that the catalyst has a different catalytic behavior after the two treatments. In particular a strong decrease in surface acidity (formation of propylene) occurs after using the catalyst in the ammoxidation of toluene, while the dehydrogenative property (formation of acetone) increases with respect to only the calcined catalyst.

Another phenomenon observed in the figure is the decrease of both acetone and propylene formation as the time of exposure to the flow of alcohol increases, until a constant behavior has been obtained, after about 1 h. A similar phenomenon has been explained by Fikis *et al.* (*31*) by a modification of the surface sites, occupied by H or OH groups on desorption of the products. This same behavior also was observed for all catalysts tested. Shown in Fig. 5 are the constant values of productivity in acetone, at 200°C, for the three different samples tested: the 5, 10, and 25% V_2O_5/TiO_2 catalysts, after use in the ammoxidation of toluene. The productivity in propylene is not shown because very small amounts of this product were obtained.

DISCUSSION

Chemical–Physical Characterization of V/Ti/O Catalysts Prepared by Flash-Drying

Chemical analyses of the calcined samples showed the presence of different kinds of vanadia species: a species that can be dissolved by the treatment with the basic solution, and two species which cannot be dissolved. The nature of these different species will be analyzed in more detail in the following sections.

Soluble V(V). The vanadium species that can be dissolved is probably characterized by a weak interaction with the support. In agreement with this, the technique of dissolution of excess vanadium has been used by some authors to prepare V/Ti/O catalysts characterized by the presence of only the monolayer (*13–15, 26*).

The IR spectrum of the untreated 25% V_2O_5/TiO_2 sample shows the presence of a weak absorption at 1020 cm^{-1} (related to the stretching frequency of V=O in V_2O_5), which disappears after washing. X-ray analyses of samples before washing do not show the lines relative to crystalline V_2O_5. Therefore the soluble vanadium (V) must be present as an amorphous V_2O_5. Only when calcination is carried out at temperatures as high as 500°C is crystalline V_2O_5 formed, as shown by the X-ray diffraction analyses and the chemical analyses.

Insoluble V(IV). The presence of a reduced V(IV) species, in relatively high amounts, after calcination at 400°C, indicates that this valence state is stabilized by some sort of strong interaction with the support. It is, in fact, well known that, for instance, V_2O_4 oxidizes to V_2O_5 at much lower temperatures. This stabilization can derive from the formation of a solid solution of V(IV) in the titania matrix, or through the formation of a strong bond between the surface Ti ions and the V(IV).

The latter hypothesis is more probable, on the basis of the fact that X-ray analysis does not show any modification of the lattice parameters of anatase.

It has been suggested that in the preparation of V/Ti/O catalysts by the grafting method a reaction between surface hydroxy groups of anatase and vanadium occurs, leading to the formation of a V–O–Ti bond (*16, 17*). In our case, the precipitation by hydrolysis of Ti and V oxohydrates from the solution containing both Ti and V(IV) ions, and the subsequent calcination treatment, probably leads to the reaction of hydroxy groups of titanic acid and of vanadium, giving rise to the insoluble V(IV). This also explains the greater amount of insoluble vanadium obtained with this preparation as compared with that obtained with wet impregnation (*15, 19*). The much greater hydroxylation of a freshly precipitated oxo-hydrate, with respect to TiO_2, leads to a large amount of vanadia species chemically bound to the support.

Figure 1 shows that the ratio between the two insoluble species V(IV) and V(V) decreases as the nominal content of vanadia increases. Thus, at low vanadia contents, the species mainly present is a V(IV) species. As the content of vanadia increases, the latter species tends toward a plateau, while V(V) increases linearly. The maximum value of the V(IV) species is very near to the value necessary for monolayer coverage (dotted lines in Fig. 1) in correspondence to the surface area of the sample. This value has been indicated by Bond and Bruckman (*17*) and by Roozeboom *et al.* (*14*) as approximately 0.14% by weight of V_2O_5, per square meter of the support. This fact suggests that the V(IV) species, stabilized against oxidation, forms a first coverage of the support. Thermogravimetric tests showed that this species can be reduced to V(III) although it is stabilized as regards its oxidation. This means that it is accessible to reactants in the gas phase, probably not occluded in the TiO_2 matrix. The infrared spectrum of the 5% sample is characterized by an absorption band at 940 cm^{-1}. Chemical analyses shows that the vanadium is mainly present as V(IV), and therefore it is reasonable to assign the band found around 940 cm^{-1} to this species. Bands in this region have not been reported in the scientific literature for V–Ti–O systems, while it has been reported that they are present in reduced vanadium oxides phases (*32*). This is in agreement with the fact that V–Ti–O catalysts prepared by impregnation do not present large amounts of reduced vanadium species (*5, 6, 17, 19, 21*).

Chemical analyses of the samples after reaction and subsequent reoxidation show that modification of the relative distribution of the different vanadia species occurs during permanence in the reactive atmosphere. In particular, the amount of unoxidable V(IV) increases for the 5 and 10% V_2O_5 samples, while it remains approximately constant for the 25% V_2O_5 catalyst.

It is interesting that the amount of V(IV) in the 10% V_2O_5 sample after reaction is close to the theoretical amount necessary for the formation of the monolayer (see Table 1). If we assume that the V(IV) species constitutes a first layered coverage of the support, this means that during the reaction a part of the insoluble V(V) species (which after reaction is present in a smaller amount), is reduced to V(IV) and spreads over the free anatase surface. In this way it contributes to completing the coverage of the support, becoming stabilized in the reduced valence state. The same occurs for the 5% V_2O_5 sample, which, however, has a global amount of V_2O_5 which is not sufficient to lead to a complete monolayer coverage. On the contrary, the phenomenon does not occur for the 25 and 10% calcined at 500°C which already, before reaction, have amounts of insoluble V(IV) species close to the theoretical amount for complete monolayer coverage (see Table 1). The latter sample, before reaction, already has undergone a strong modification of the relative amounts of the different vanadia species. This occurs in correspondence with the decrease in the surface area caused by the calcination treatment (see Table 1).

Insoluble V(V). The third species identified by the chemical analyses is a V(V) species insoluble in ammonia solution. It is the prevailing species only at relatively high vanadia contents and seems to increase practically linearly with increasing nominal V_2O_5. The IR spectrum of the 25% V_2O_5 sample is characterized by an absorption band around 980 cm^{-1}. Since most of the interacting vanadium is present as V(V) in the calcined 25% V_2O_5 catalyst (see Fig. 1), we can correlate the observed absorption to this species. The IR spectrum of the 10% V_2O_5 catalyst, which represents an intermediate chemical situation between the 5 and the 25% V_2O_5 samples, shows an intense absorption at 950 cm^{-1}.

Thermogravimetric tests indicated that this species is very easily reducible to V(IV). This is in agreement with the results of other authors who indicated that the monolayer of vanadia spread over TiO_2 surface contains more reactive species than the bulk vanadia (*5*, *14*).

The lower frequency of stretching for V(V), compared to that at 1020 cm^{-1} for V=O in crystalline V_2O_5, indicates a lower bond strength for the V=O bond, thus explaining its high reactivity, as indicated by the reduction tests in the thermobalance. Also, in the case of partially reduced V_2O_5, or of some suboxides such as V_6O_{13} or V_4O_9, the appearance of bands in the 950–1000 cm^{-1} region has been attributed to weakened V=O bonds (*8*, *32–34*).

Moreover, our data agree with some of the reported results about the chemical–physical characterization of the monolayer. It has been suggested that the V(V) ion constituting the monolayer in catalysts prepared by wet impregnation or grafting is characterized by an IR absorption at 980 cm^{-1}, as long as there is a Raman feature in the same region (*5*, *14*, *15*, *25*, *35*).

The peculiarities of this species are (a) during the reaction, it is almost all reduced; in fact analysis of the spent catalysts showed practically no insoluble V(V) species (see Table 1). (b) It is an unstable species; in fact after catalytic reaction and reoxidation, the global amount of this species is reduced with its transformation into V_2O_5 and to the not reoxidizable V(IV). Also, calcination in air at 500°C strongly reduces the amount of this species which is transformed into crystalline V_2O_5.

Correlation between Activity and Vanadia Species

Shown in Fig. 7 is a correlation between the activity in benzonitrile and nitrogen formation and the amounts of the different vanadia species identified in the catalysts after reaction and reoxidation (taken from Table 1). In particular, the benzonitrile and N_2 productivities are plotted against the V(IV) and V(V), respectively. The existence of fairly good linear correlations indicates that the two different vanadia species are responsible for the two different reactions. Thus, the V(IV) centers are reoxidizable seem to be the active sites responsible for alkyl-aromatic activation (and therefore the formation of benzonitrile). The V(IV)

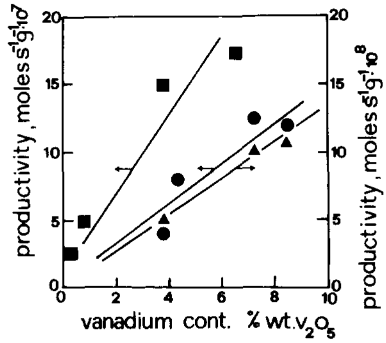

FIG. 7. Correlation between the productivity in benzonitrile (●) and the amount of unoxidizable V(IV) in spent catalysts, between the productivity in nitrogen (■) and the amount of V(V) in spent and reoxidized catalysts, and between the productivity in acetone (▲) and the amount of unoxidizable V(IV). The productivities are deduced from Fig. 5.

species reoxidizable in air (measured as insoluble V(V) species), instead, seem to be the sites responsible for combustion of ammonia to nitrogen.

This correlation explains the similar activities of the 10 and 25% V_2O_5 samples in the formation of benzonitrile (see Fig. 5), as well their different activity in the combustion of ammonia. In fact the two samples have similar amounts of unoxidizable V(IV) centers after reaction, and different amounts of insoluble V(V).

In agreement with this hypothesis is also the catalytic behavior of the 10% V_2O_5 sample calcined at 500°C. Chemical analyses indicate that the sample has a greater amount of insoluble V(V) and a lesser amount of insoluble V(IV) after reaction as compared with the sample calcined at only 400°C. Correspondingly, the sample exhibits a higher activity in ammonia combustion, and a lower one in the conversion of toluene. Moreover, similarly, the nonstable catalytic behavior of the samples in the first hours of reaction reflects the modification of the chemical situation occurring during this period. In particular, in correspondence with an increase in the insoluble V(IV) species for the 10% V_2O_5/TiO_2 sample, an increase in the yield of benzonitrile is observed (Fig. 4), while a decrease of the insoluble V(V) species is accompanied by a decrease in the formation of nitrogen from the combustion of ammonia.

Similar results are obtained in the case of alcohol dehydrogenation to acetone. Figure 7 shows that a direct correlation exists between the number of unoxidizable V(IV) sites in the sample and the productivity of acetone (the latter deduced from the data shown in Fig. 5). A further confirmation comes from the activity in acetone formation for the 10% V_2O_5/TiO_2 sample, after calcination, as compared to the activity after it had been used in toluene ammoxidation (Fig. 6); an increase in the dehydrogenation property is observed, along with a corresponding increase in the amount of insoluble V(IV). The fall in acidity (propylene formation) is explained by a neutralization exercised by ammonia on acidic sites.

In conclusion, the V(IV) centers that, according to our model, can be located in a first layer coverage of the TiO_2, constitute the active sites in both dehydrogenation of the alcohol, and in the removal of the H species from the methyl group in toluene (slow step in toluene ammoxidation). The presence of insoluble V(V) sites leads instead to the formation of active sites in the undesired reaction of ammonia combustion.

CONCLUSIONS

Surface Mode of V/Ti/O Catalysts Prepared by Flash-Drying

On the basis of the reported results, the model shown in Fig. 8 is suggested for the V/Ti/O catalytic systems prepared by flash-drying. It considers the presence of a first layer of V(IV) sites, in direct contact with the anatase surface. These sites are stabilized as regards oxidation, but can be reduced to V(III).

Some sort of structure containing V(V) sites must be formed above the first layer of V(IV). In the model, this insoluble structure is represented in the morphology of

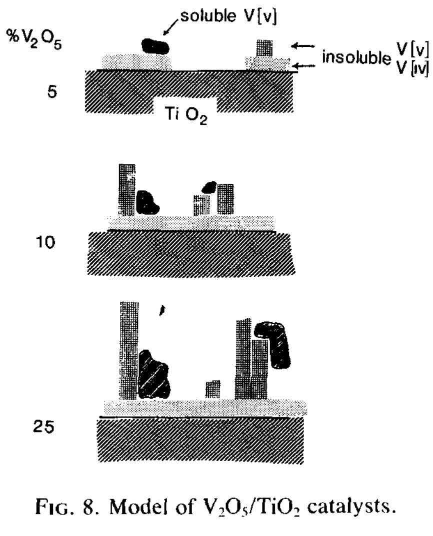

FIG. 8. Model of V_2O_5/TiO_2 catalysts.

"towers," in agreement with that recently suggested by Bond *et al.* (*20*). Catalytic data, in fact, indicate that the active sites for toluene activation and alcohol dehydrogenation are the V(IV) centers which, according to our model, are located in the first layer of vanadium oxide. Therefore, the insoluble V(V) must be organized in a structure that does not cover the first layer, but leaves it accessible to the reactants in the gas phase. The model reported by Inomata *et al.* (*13*) deals instead with the presence of multilayers of vanadium oxide over the support. The insoluble V(V) species is characterized by a high reducibility to V(IV). Moreover, it contains the active sites for the combustion of ammonia to nitrogen.

A comparison with the models reported for V/Ti/O catalytic systems prepared by the more classic methods of wet impregnation or grafting shows both analogies and differences. First, in the present case the interacting vanadium is much larger than in the samples prepared with the other techniques cited (*15, 19*). This difference can be attributed to the greater degree of hydroxylation of the titanic acid as compared to the TiO_2. Moreover, it has been established in the literature that the monolayer of vanadium oxide consists mainly of V(V) ions (*5, 6, 17, 21*), even though it has been reported that a fraction of interacting vanadia is present also as V(IV) (*8, 13, 15, 19, 36*); the weakly interacting vanadium oxide (the main fraction) is present instead only as V(V) (*19*).

Our data indicate, on the contrary, that in V/Ti/O catalysts prepared by flash-drying, a considerable fraction of the interacting vanadium is in the reduced state, above all at small vanadia contents. This difference can be related to the present preparation methodology, which is very different from the one generally employed. Moreover, we start from a solution containing V(IV) ions, rather than V(V) ions, thus explaining the higher average degree of reduction of our samples.

ACKNOWLEDGMENTS

Support of this work by the "Ministero Publica Istruzione—Gruppo Nazionale Struttura e Reattività delle Superfici" is gratefully acknowledged.

REFERENCES

1. van der Berg, P. J., van der Wiele, K., and den Ridder, J. J., *in* "Proceedings 8th International Congress on Catalysis, Berlin, 1984," Vol. V, p. 393. Dechema, Frankfurt-am-Main, 1984.

2. van Hengstum, A. J., van Ommen, J. G., Bosch, H., and Gellings, P. J., *Appl. Catal.* **8,** 369 (1983).

3. Cole, D. J., Cullis, Ch. F., and Hucknall, D. J., *J. Chem. Soc. Faraday Trans. I* **72,** 2185 (1978).

4. Vanhove, D., and Blanchard, M., *J. Catal.* **36,** 6 (1975).

5. Wachs, I. E., Saleh, Y., Chan, S. C., and Chersich, C. C., *Appl. Catal.* **15,** 339 (1985).

6. Saleh, R. Y., Wachs, I.E., Chan, S. S., and Chersich, C. C., *J. Catal.* **98,** 102 (1986).

7. Andersson, A., *J. Catal.* **76,** 144 (1982).

8. Andersson, A., and Andersson, S. L. T., *in* "Solid State Chemistry in Catalysis" (R. K. Grasselli and J. F. Brazdil, Eds.), ACS Symp. Series 279, p. 121. 1983.

9. Suvorov, B. V., Gutsalyuk, G. N., and Bukeikanov, N. R., *Akad. Nauk. Kaz. SSR Ser. Khim.* **22**(2), 87 (1972).

10. Cavalli, P., Cavani, F., El-Sawi, M., Manenti, I., and Trifirò, F., *Ind. Eng. Chem. Res.* **26,** 804 (1987).

11. Cavalli, P., Cavani, F., Manenti, I., and Trifirò, F., *Ind. Eng. Chem. Res.* **26,** 639 (1987).

12. Cavalli, P., Cavani, F., Manenti, I., and Trifirò, F., *Catalysis Today* **1,** 245 (1987).

13. Inomata, M., Mori, K., Miyamoto, A., Ui, T., and Murakami, Y., *J. Phys. Chem.* **83,** 754 (1983).

14. Roozeboom, F., Mittelmeijer-Hazeieger, M. C., Mouljin, J. A., Medema, J., de Beer, V. H. J., and Gellings, P. J., *J. Phys. Chem.* **84,** 2783 (1980).

15. Busca, G., Genti, G., Marchetti, L., and Trifirò, F., *Langmuir* **2,** 568 (1986).

16. Busca, G., Marchetti, L., Centi, G., and Trifirò, F., *J. Chem. Soc., Faraday Trans. I* **81,** 1003 (1985).

17. Bond, G. C., and Bruckman, K., *Faraday Disc.* **72**(14), 235 (1981).

18. Meriaudeau, P., and Vedrine, J. C., *Nouv. J. Chim.* **2,** 133 (1978).

19. Cavani, F., Centi, G., Parrinello, F., and Trifirò, F., *in* "Preprints, 4th Int. Symp. on Scientific Bases for the Preparation of Heterogeneous Catalysts, Louvain-la-Neuve, September 1986."

20. Bond, G. C., Zurita, J. P., Flamerz, S., Gellings, P. J., Bosch, H., van Ommen, J. G., and Kip, B. J., *Appl. Catal.* **22,** 361 (1986).

21. Haber, J., *Pure Appl. Chem.* **56**(12), 1663 (1984).

22. Vejux, A., and Courtine, P., *J. Solid State Chem.* **23,** 83 (1978).

23. Gasior, M., Gasior, I., and Grzybowska, B., *Appl. Catal.* **10,** 87 (1984).

24. Iwamoto, M., Furukawa, H., Matsukami, K., Takenaka, T., and Kagawa, S., *J. Amer. Chem. Soc.* **105,** 3719 (1983).

25. Nakagawa, Y., Ono, T., Miyata, H., and Kubokawa, Y., *J. Chem. Soc. Faraday Trans. I* **79,** 2929 (1983).

26. Yoshida, S., Iguchi, T., Ishida, S., and Tarama, K., *Bull. Chem. Soc. Japan* **45,** 376 (1972).

27. Niwa, M., and Murakami, Y., *J. Catal.* **76,** 9 (1982).

28. Cavani, F., Centi, G., Manenti, I., and Trifirò, F. *Ind. Eng. Chem. Prod. R&D* **24,** 221 (1985).

29. Busca, G., Cavani, F., Centi, G., and Trifirò, F., *J. Catal.* **99,** 400 (1986).

30. Dyakova, B., Mehandzhiev, B., Grzybowska, B., Gasior, I., and Haber, J., *Appl. Catal.* **3,** 255 (1982).

31. Fikis, D. V., Murphy, W. J., and Ross, R. A. *Canad. J. Chem.* **57,** 2464 (1979).

32. Andersson, A., Wallenberg, R., Lundin, S. T., and Bovin, J. O., *in* "Proceedings 8th International Congress on Catalysis, Berlin, 1984," Vol. 5, p. 381. Dechema, Frankfurt-am-Main, 1984.

33. Theobald, F., *Rev. Roum. Chim.* **23,** 887 (1978).

34. Clauws, P., and Verhand, K. *Acad. Wet. Lett. Schone Kunsten Belg. K£. Wet.* **42,** 102 (1980).

35. Bond, G. C., Sarkani, A. J., and Parfitt, G. D., *J. Catal.* **57,** 476 (1979).

36. Rusiecka, M., Grzybowska, B., and Gasior, M., *Appl. Catal.* **10,** 101 (1984).