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Surface Acidity of Silica–Titania Mixed Oxides

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A study of the acidity of coprecipitated SiO_2–TiO_2 oxides is presented. The amount of acidity has been determined by ammonia adsorption at 150°C. The acidity was also characterized by TPD of adsorbed ammonia and by infrared spectroscopy of various adsorbed probes, such as pivalonitrile, pyridine, ammonia, and *n*-butylamine. From the quantitative measurements of adsorption of ammonia and from TPD it was concluded that the SiO_2–TiO_2 mixture can be regarded as a mechanical mixture of silica and titania. However, the IR investigation showed that Ti enters in small amounts into the silica framework. This results in formation of very strong Lewis acid sites, caused by incomplete tetrahedral coordination of Ti^{4+} ions exposed on the surface. © 1992 Academic Press, Inc.

INTRODUCTION

Mixed oxides frequently have better catalytic properties than the pure oxide components. In particular, it has been found that mixed oxides can develop very strong acidity even when the pure oxide components do not show it (*1*, *2*). The best known case is that of silica–aluminas, which have been widely used for decades as acidic catalysts, being far stronger acids than both pure silica and pure alumina. At least three different theories have been developed to justify the enhanced acidity of mixed oxides (*3–5*).

Recently, increasing interest has been devoted to silica–titania mixed oxides. Materials belonging to this system have been found to be even more acidic than silica–aluminas (*6*). Similar materials have been found to be very good catalysts for the combustion of 1,2-dichloroethane (*7*) and have also been used for the ammoxidation of toluene, probably catalyzed by surface carbonaceous materials (*8*). In both cases the catalytic activity has been correlated with the surface acidity. Moreover, silica–titanias have been tested as supports for several kinds of catalysts, such as Ni for CO hydrogenation (*9*) and chromia for ethylene polymerization (*10*), and they appear to be especially optimal supports for vanadia-based catalysts for NO_x reduction by ammonia (*11–14*). This is because they appear to combine the mechanical properties of silica and the chemical properties of the active support titania. In this respect, the development of very strong acidic properties when silica and titania are chemically mixed can be undesirable. In a recent paper (*14*), silica–titania mixed oxides produced by coprecipitation have been characterized from the point of view of the bulk and surface structure. We report here the results of a characterization study of the surface acidity of these materials.

EXPERIMENTAL

The preparation of the mixed oxides, starting from solutions of Na_2SiO_3 and $TiCl_4$, and their bulk and textural characterization have been reported previously (*14*). Some properties of the oxides, calcined for 1 h at 450°C, are listed in Table 1.

The FT-IR spectra were recorded using a Nicolet 5ZDX instrument. Self-supporting pressed disks were evacuated at 360°C be-

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TABLE 1

Composition and Surface Areas of Silica–titania Samples

Notation	TiO_2 content (mol%)	S_{BET} (m^2/g)
A	0.0	342
B	0.5	386
C	10.0	327
D	25.0	311
E	50.0	268
F	50.0	235
G	75.0	234
H	90.0	253
I	99.5	132
K	100.0	122

fore adsorption experiments in a conventional heatable IR cell connected to a greaseless vacuum/gas manipulation line.

Quantitative measurement of the adsorption of ammonia was performed by the frontal method (*36*) in a HP 5890A gas chromatograph. The gases, ≥99.9990% N_2 (≤2 ppm O_2) and 1.5% NH_3 in the same N_2, were dosed by massflow regulators. A flow of 60 ml/min (STP) of both gases passed through separate heated tubes via a four-port valve, either to the sample or to waste. The sample, 0.2 g of the screened fraction between 0.710 and 0.425 mm, was placed in a ¼-in. stainless-steel tube inside the chromatograph oven. Each sample was degassed for 1 h at 400°C in a flow of 60 ml/min (STP) pure N_2 before adsorption of ammonia. Then the temperature was lowered to 150°C. When the temperature and the chromatographic baseline had become stable, the gas flow was switched from pure N_2 to 1.5% NH_3 in N_2. A breakthrough curve was obtained, followed by a plateau as shown in Fig. 1. After 20 min the gas was switched back to pure N_2 (at time *B* in Fig. 1). This results in an elution curve of reversibly adsorbed ammonia. From this curve it was possible to determine the reversibly adsorbed amount, but since the rear profile was often tailing, a renewed adsorption was conducted when the baseline had returned to the origin. In this way the reversibly adsorbed amount of ammonia was determined from the front profile of the second adsorption performed as the first one. After the second adsorption the sample was flushed with pure N_2 for 1 h. Then a TPD profile was recorded while the oven temperature was increased from 150 to 400°C (the maximum temperature usable for this GC) with a rate of 15°C/min under a flow of 60 ml/min (STP) of pure N_2.

RESULTS

(*a*) *FT–IR Study of the Adsorption of Pivalonitrile*

In previous papers it has been shown that very weak bases such as nitriles can be very useful for the characterization of strong Lewis acid sites (*15*, *16*). The CN stretching frequency is sensitive to the electron withdrawing strength in an acid–base interaction involving the lone pair electrons of the N atom of nitriles.

The CN stretching band is shifted toward higher frequency with respect to the liquid-phase value. Acetonitrile is a useful probe, but its νCN band is split due to a Fermi resonance with a νCC + δCH_3 mode (*15*). In contrast, the νCN band of pivalonitrile (2235 cm^{-1} in the liquid (*15*, *17*)) is single, allowing a better examination of its behavior upon acid–base interaction. Moreover, it has been shown that nitriles can also phy-

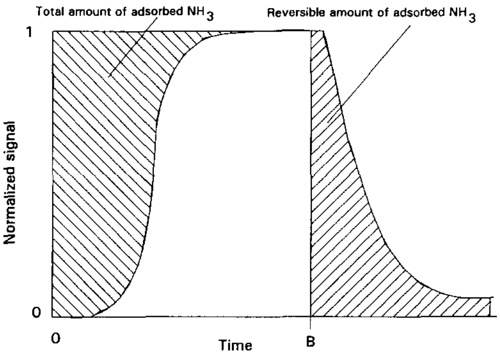

FIG. 1. Adsorption of ammonia by the frontal method. Injection of 1.5% NH_3 in N_2 starts at time 0, and at time *B* the flow is changed to pure N_2.

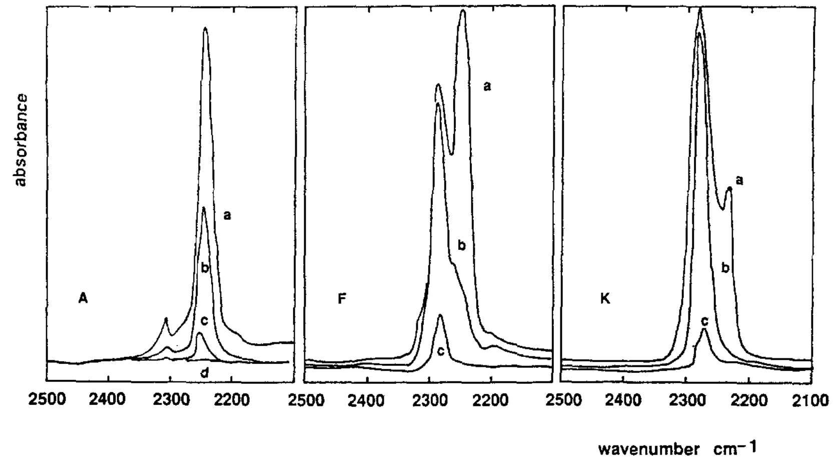

FIG. 2. FT-IR spectra (νCN region) of pivalonitrile adsorbed on sample A (100% SiO_2) [in contact with PN vapor, 0.1 Torr (a), and under evacuation at room temperature for 5 min (b), 15 min (c), 30 min (d)], on sample F (50% TiO_2) [in contact with PN vapor 0.1 Torr (a), and under evacuation at room temperature for 30 min (b) and at 167°C for 30 min (c)], and on sample K (100% TiO_2) [in contact with PN vapor 0.1 Torr (a), and under evacuation at room temperature for 30 min (b) and at 167°C for 30 min (c)].

sisorb on surface OH groups, the νOH band of which shifts more to lower wavenumber the stronger their acidity (*18*). Hence, pivalonitrile can be used as a probe for both Lewis and Brønsted acidity.

The spectrum of pivalonitrile (PN) adsorbed on sample A (100% SiO_2) in the νCN region shows a single strong band at 2245 cm^{-1} (Fig. 2A). This band is due to νCN of PN molecules interacting with surface silanol groups through the N lone pair. The small shift to higher wavenumber with respect to the liquid is an effect of the electron withdrawal arising from this H bond. Only at very high coverages is a very small band observed at 2308 cm^{-1}, due to a combination band (2307 cm^{-1} in the liquid (*17*)). Evacuation at room temperature causes progressive and ultimately complete disappearance of adsorbed PN.

The spectrum of PN adsorbed on sample K (100% TiO_2, Fig. 2 K) at very high coverages shows a very strong νCN band at 2280 cm^{-1}, having a shoulder near 2290 cm^{-1} and a weaker band at 2235 cm^{-1}. The position of the two higher-frequency components indicates that they are very likely due to PN molecules coordinated on Ti^{4+} cations, being significantly perturbed as a result. The slight splitting of this band (2285, 2260 cm^{-1}) is in line with the data obtained by CO adsorption on these samples (*14*). In fact, CO adsorption on K (100% TiO_2) shows that two different cationic sites responsible for the formation of two different carbonyl species giving two νCO bands are present, as generally found on anatase preparations. Thus the bands at 2285 and 2260 cm^{-1} are assigned to PN molecules coordinated through the N lone pair to Ti^{4+}-exposed ions having two and one coordinative unsaturations, respectively, with respect to the octahedral coordination of titanium ions in the anatase bulk (*19, 20*). This interpretation agrees with the stability of the adsorbed species. The species responsible for the component at 2260 cm^{-1} is more labile than that absorbing at 2285 cm^{-1}. However, this apparently contradicts the information from the band intensities. In the case of adsorbed PN the component due to species interacting with the stronger site (2285 cm^{-1}) is at saturation more intense than that related to species bonded to the weaker sites (2260 cm^{-1}). In the case of adsorbed CO the opposite is observed (*14, 19*). However, the extinction coefficient, both of νCN of pivalonitrile and of νCO of adsorbed carbon monoxide, depends on the strength of the adsorption bond. It seems likely that the polarizability of the CN bond of nitriles is higher than that of CO. If this is so, the extinction coefficient of νCN of nitrile can be more sensitive to the strength of the coordination bond than νCO of carbon monoxide, thereby being much enhanced in the case of the 2285 cm^{-1} species with respect to that of the 2260 cm^{-1} species. This presumed higher sensitivity of the extinction coefficient of nitriles with respect to CO could well justify the observed inversion of the relative intensities of the respective adsorbed species. The third weaker band, detected after PN adsorption at nearly the same frequency where the νCN band of the liquid falls, is assigned to physisorbed species, possibly interacting with very weakly acidic OH groups. According to these assignments, the stability of the three species is proportional to the perturbation (shift upward) of the νCN frequency. In any case, the bands due to PN bonded on Lewis sites do not disappear even by evacuation at 440 K (Fig. 2 K(c)).

The spectra of PN adsorbed on samples D–I (25–99.5% TiO_2) contain both the features of PN adsorbed on the silanol groups (a band near 2245 cm^{-1} with a very weak band near 2308 cm^{-1} only at very high coverages), easily desorbed by evacuation at room temperature, and on Ti^{4+} groups of titania (a band near 2285 cm^{-1}), resistant to evacuation at room temperature (see Fig. 2F for sample F (50% TiO_2)). As expected, these features have different relative intensities in rough dependence on the SiO_2 : TiO_2 composition of the samples.

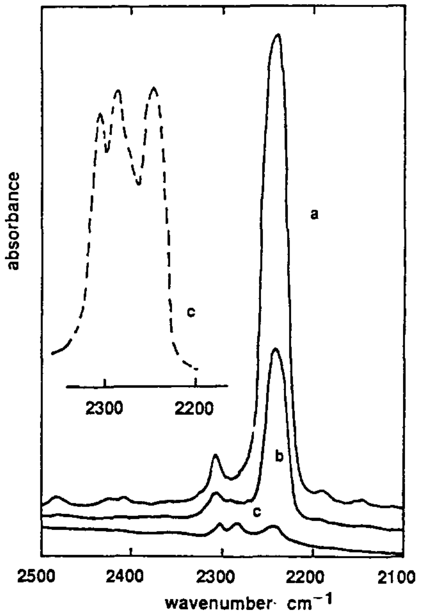

FIG. 3. FT–IR spectra (νCN region) of pivalonitrile adsorbed on sample C (10% TiO_2) [in contact with PN vapor, 0.1 Torr (a), and under evacuation at room temperature for 5 min (b) and 15 min (c)].

However, in the case of sample C (Fig. 3, 10% TiO_2) at very low coverages a further component is observed at 2308 cm^{-1}, more stable to evacuation than the others. Although this band coincides with a band appearing only at very high coverages on all samples and already assigned to a very weak combination band, it is certainly due to the νCN fundamental of a new PN species. In fact it is detected even after long time evacuation, with an intensity comparable to that of νCN of the other adsorbed species. On the basis of both the very strong shift to higher frequency of the νCN band and its very strong stability to evacuation, this species must be coordinated to very strong Lewis sites. In Table 2 the positions of the νCN band of PN adsorbed on different solids are compared. It is evident that the sites responsible for this band, although probably in a small amount according to the very small intensity of this band, are extremely strong and characterize this sample as one of the most acidic solids as far as the strength of sites is concerned.

This result accords with those arising from CO adsorption. In sample C (10% TiO_2) a νCO band has been detected at an unusually high frequency (*14*). This has been interpreted assuming that Ti^{4+} can enter into the silica network in a tetrahedral

TABLE 2

Position (cm^{-1}) of the νCN Band of Adsorbed Pivalonitrile on Different Solids

Solid	νCN of adsorbed pivalonitrile	Reference
AlF_3	2309, 2305	t.w.
SiO_2–TiO_2 (sample C)	2308	t.w.
Fluorided Al_2O_3	2301	(*38*)
γ-Al_2O_3, δ-Al_2O_3	2296	(*14*)
$SiO_2Al_2O_3$ (87 : 13)	2295	t.w.
η-Al_2O_3	2292	(*38*)
SiO_2–Al_2O_3 (50 : 50)	2292	(*38*)
TiO_2 (sample K)	2285, 2260	t.w.
SiO_2–TiO_2 (samples D–I)	2285	t.w.
MgO	2260	(*38*)
SiO_2 (sample A)	2245	t.w.
Liquid	2236	(*17*)

Note. t.w., this work.

coordination. Some of these ions can remain on the surface and be coordinatively unsaturated, thereby being available for CO coordination. The presence of silica can be useful to induce such an unusual coordination of Ti^{4+}, which, in oxidic environments, generally prefers octahedral coordination. However, there are no electronic reasons for excluding tetrahedral coordination for a d_0 ion such as Ti^{4+}.

As already cited, pivalonitrile adsorption can also be used to check the Brønsted acidity of solids through the measure of the shift of the νOH band of acidic OH groups. In Fig. 4 are reported the spectra of A and C (100% SiO_2 and 10% TiO_2), respectively, both obtained after PN adsorption at high coverages (0.1 Torr pressure in static conditions) and ratioed with respect to the spectrum of the pure catalyst after activation. In these spectra the sharp νOH bands of the free OH groups as they are present in the spectrum of the activated sample (3745 cm^{-1}) are observed as a negative-signal, because they disappear upon PN adsorption, while the broader bands due to νOH of the hydroxy groups involved in H bonding with PN appear positive, at lower frequencies. The bands of species that are not perturbed by interactions (such as the skeletal bands of the solid) are subtracted and do not appear at all. The extent of the shift toward lower frequencies of the νOH bands upon H bonding depends on the strength of this interaction. In our case, the position of the band of the surface hydroxy groups upon H bonding with PN molecules can be taken as a measure of their Brønsted acidity. These bands are centered near 3350 cm^{-1} on sample A, near 3300 cm^{-1} on sample C, while on samples containing more TiO_2 they shift again to higher frequencies (near 3440 cm^{-1}). This indicates that surface Brønsted sites are stronger in sample C than in sample A and are definitely weaker in samples with high TiO_2 contents.

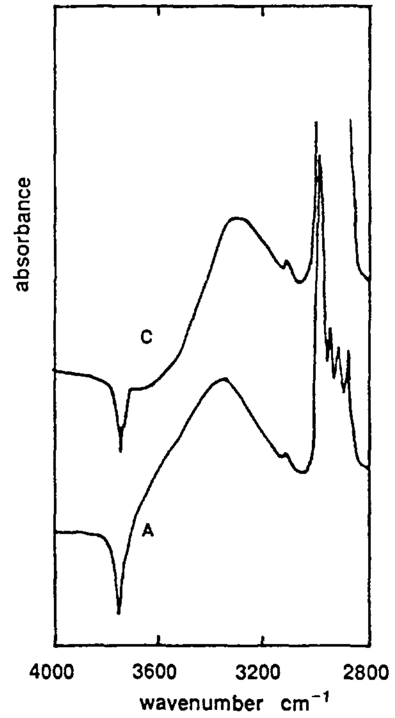

FIG. 4. Subtraction FT–IR spectra of samples A (SiO_2) and C (10% TiO_2) upon pivalonitrile adsorption showing the perturbation of the νOH bands. The spectra have been recorded in the presence of pivalonitrile vapor (0.1 Torr) but the contributions of both pivalonitrile gas and the activated catalyst have been subtracted.

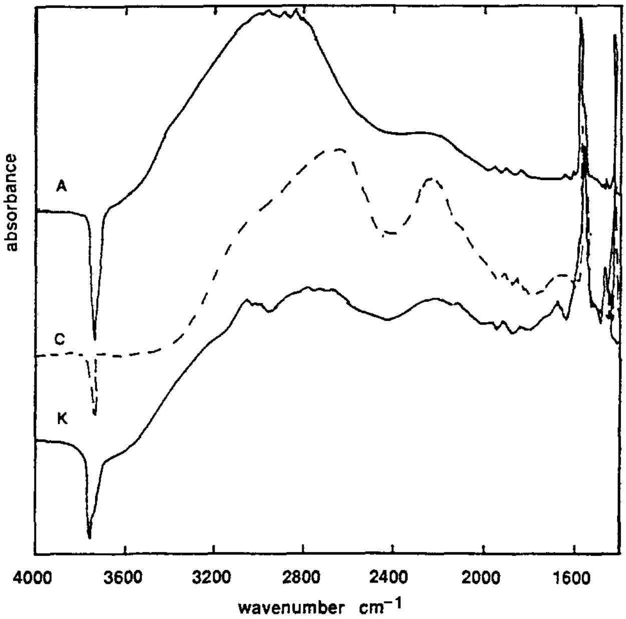

FIG. 5. Subtraction FT–IR spectra of samples A (SiO_2), C (10% TiO_2) and K (50% TiO_2) upon pyridine adsorption showing the perturbation of the νOH bands. The spectra have been recorded in the presence of pyridine vapor (0.1 Torr) but the contributions of both pyridine vapor and the activated catalyst have been subtracted.

(*b*) *FT–IR Study of the Adsorption of Pyridine, Ammonia, and n-Butylamine*

The spectra of pyridine (Py) adsorbed on A (100% SiO_2) are consistent with the results previously reported for Py/silica interaction. Py only physisorbs via H bonding on the surface silanol groups, leading to species characterized by bands at 1595, 1580 (weak), 1490, and 1445 cm^{-1} (8a, 8b, 19b, and 19a vibrational modes, respectively, according to the notation of Wilson (*21*)). The νOH band of surface hydroxy groups (Fig. 5A) perturbed by H bonding is observed much broadened near 2950 cm^{-1}, according to the shift of about 800 cm^{-1} reported by several authors (*22, 23*). However, we also note a second broad component near 2300 cm^{-1}. The spectrum of Py adsorbed on C (10% TiO_2) is very similar to that of Py on A in the region of the ring vibration modes, although weak components near 1610 and 1450 cm^{-1} probably arise from the 8a and 19b vibrational modes of Lewis-bonded Py. The bands associated with the vibrations of the surface OH groups, perturbed by Py adsorption (Fig. 5C), are instead very different on C with respect to A. In the case of C, in fact, the broad component near 3000 cm^{-1} is evident only as a weak shoulder, while two very strong components are evident centered near 2700 and 2300 cm^{-1}, with a window at 2450 cm^{-1}. These features are typical of very strong H bonding (*24, 25*), where the OH stretching mode, shifted strongly to lower frequency, gives a very strong Fermi resonance with the first overtone of the deformation mode, that is shifted upward. The broad weak component observed near 2300 cm^{-1} also for the system Py/sample A is probably associated with a similar H-bonding system. The difference between the spectra relative to Py adsorption on A and C indicates that very weakly acidic silanol groups are predominant on A while silanols that are slightly more acidic

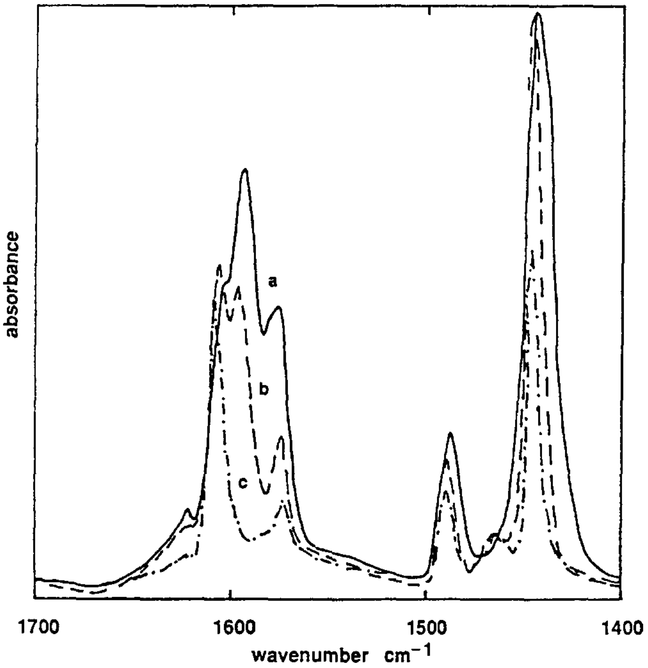

FIG. 6. FT-IR spectra of pyridine adsorbed on sample F (50% TiO_2) in contact with Py vapor 0.01 Torr (a) and after evacuation for 30 min at room temperature (b) and at 197°C (c).

are predominant on C. However, none of them are able to protonate Py, since pyridinium cations are not detected at all.

On the samples having a higher titania content (see Figs. 5K and 6 for sample F (50% TiO_2)), features of Py both chemisorbed on Lewis sites and H-bonded on surface silanols are detected. Pyridine coordinated on Lewis sites is characterized by bands at 1610, 1575, and 1492 cm^{-1}, corresponding to the 8a, 8b, and 19b vibrational modes of Py. The 19a component appears instead to be weakly split (components near 1450 and 1446 cm^{-1}). These bands are also present on pure titania (sample K). However, on the samples also containing silica, the features relative to H-bonded pyridine (in particular the ν8a band near 1595 cm^{-1}, Fig. 6a) and the corresponding broad νOH/δOH absorptions discussed above (Fig. 5K) are detected, although they are weak. The results concerning Py adsorption confirm the above data showing that: (i) Lewis sites are associated with Ti^{4+} cations present on the surface of titania and all titania-containing materials; (ii) very weakly acidic silanol groups are predominant on the surface of silica together with a few stronger Brønsted acid sites; (iii) relatively stronger Brønsted acidic silanol groups are present on the samples containing both silica and titania (these sites H bond Py strongly but are not able to protonate it) and; (iv) these stronger sites are present in relatively larger amounts on sample C (10% TiO_2), where silica containing Ti^{4+} ions is more predominant than on samples F–I (50–99.5% TiO_2), where silica covers bulk titania. This implies that these more acidic silanols are associated with the former phase, i.e., the saturated solid solution of titania in silica.

Analogous results are obtained using ammonia as the basic probe. To check the acid strength of surface silanols, an even stronger base also has been used as a probe, namely *n*-butylamine. The spectrum of the adsorbed species arising from butylamine adsorption on C (10% TiO_2) and F (50%

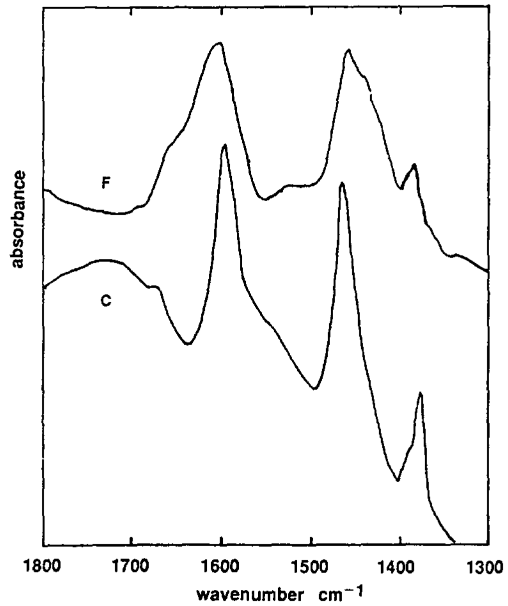

FIG. 7. FT–IR spectra of *n*-butylamine adsorbed on samples C (10% TiO_2) and F (50% TiO_2) after evacuation at room temperature for 30 min.

TiO_2) are reported in Fig. 7. The bands at 1600 (NH_2 scissoring), 1470 (CH_3 asymmetric deformation), and 1380 cm^{-1} (CH_3 symmetric deformation) are due to the base molecularly adsorbed (coordinated and H-bonded), while the very weak broad components near 1550 and 1630 cm^{-1} are due to the asymmetric and symmetric deformation modes of the *n*-butyl-ammonium cation (*26*). It is evident that the cations, arising from the protonation of the base by the Brønsted acidic protons of surface silanol groups, are present in a very small amounts. Evacuation at room temperature almost completely causes the disappearance of the features of the cations, showing that the acidity of the active silanol groups is small.

(*c*) *Studies of Ammonia Adsorption and Desorption* (*TPD*)

With the exception of the samples with 0 and 100% TiO_2, the acidic amount was determined twice with a fresh catalyst. The totally adsorbed amount of ammonia per gram passes through a maximum for sample H (90% TiO_2). In Table 3 the different types and amounts of adsorbed ammonia referred to the surface area are shown. For comparison, the acidities of the materials of Itoh *et al.* (*37*) are also given. They determined the acidic amount on coprecipitated SiO_2–TiO_2 samples with a few different TiO_2-molar ratios. The determination was conducted by titration with *n*-butylamine in benzene using different indicators. The specific acidic amounts ($\mu mol/m^2$), given in Table 3, with an acidic strength $H_0 \leq +3.3$ (*p*-dimethylaminoazobenzene as indicator) have been calculated from the data of Itoh *et al.* (*37*). They also determined the acidic amount by adsorption of NH_3 in a gravimetric equipment at 150°C, which was given as 1.56 $\mu mol/m^2$ for $SiO_2 : TiO_2$ with a molar ratio of 1 : 1. Although the adsorbed amounts are similar, it is clear that their data have a different trend from ours with a maximal specific acidity at 90 mol% TiO_2. Our results do not show this maximum. According to some theories (*3–5*), the coprecipitated SiO_2–TiO_2 should be a material with enhanced acidic properties. In that case, the material properties should significantly deviate from those of a mechanical mixture of the two oxides.

To test this hypothesis we assumed that the coprecipitated oxides behave like a mechanical mixture of SiO_2 and TiO_2. The specific amount of adsorbed ammonia can thus be calculated with the assumption that the acidic properties are additive. In Fig. 8 the experimentally determined amount of irreversibly adsorbed ammonia is plotted versus the calculated adsorbed amount at different silica/titania ratios. A linear correlation with a slope of 1.02 is obtained. This indicates that the material behaves like a mechanical mixture of the two oxides. As phases other than SiO_2 and TiO_2 are present, as indeed is the case (*14*), their abundance must be small or they do not adsorb ammonia at 150°C. The TPD profiles in the temperature range 150–400°C were used to calculate the totally desorbed amount shown in Table 3. To obtain a picture of the acidic

TABLE 3

The Adsorption and Desorption of Ammonia as a Function of the TiO_2 Content of Mixed Silica-Titanias

TiO_2 content (mol%)	Totally adsorbed NH_3 (μmol/m^2)	Irreversibly adsorbed NH_3 (μmol/m^2)	Reversibly adsorbed NH_3	Desorbed NH_3 at 400°C (μmol/m^2)	Acdity[a] $H_0 \leq 3.3$ (μmol/m^2)
0.0	0.33	0.16	0.17	0.007	0
0.5	0.40	0.17	0.24	0.045	—
0.5	0.39	0.14	0.25	—	—
10.0	0.87	0.47	0.40	0.322	1.124
10.0	0.83	0.43	0.40	—	—
25.0	1.61	1.01	0.59	0.812	—
25.0	1.64	1.07	0.57	—	—
50.0	3.02	1.98	1.04	1.422	1.967
50.0	3.00	1.97	1.04	—	1.56[b]
75.0	4.38	3.29	1.10	2.303	—
75.0	4.39	3.23	1.17	—	—
90.0	4.52	3.46	1.06	2.615	2.304
90.0	4.37	3.30	1.06	—	—
99.5	6.35	4.93	1.41	3.016	—
99.5	6.08	4.43	1.64	—	—
100.0	5.84	4.34	1.50	2.452	0.69

[a] Determined by titration with *n*-butylamine in benzene using *p*-dimethylaminoazobenzene as indicator. Calculated from (*37*).

[b] Determined by adsorption of ammonia at 150°C. Calculated from (*37*).

strength distribution, the TPD profiles for samples A, C, E, H, and K were analyzed by integrating the desorbed amount of NH_3, normalized to a totally desorbed amount at 400°C, over 50°C intervals. The result is shown in Fig. 9. The maximum in the desorption peak is changed from low temperatures (200–250°C) for the samples with high SiO_2 contents (i.e., A) to higher temperatures (300–350°C) for intermediate mixtures (C, E, H). For samples with high TiO_2 content (K), the maximum is then again

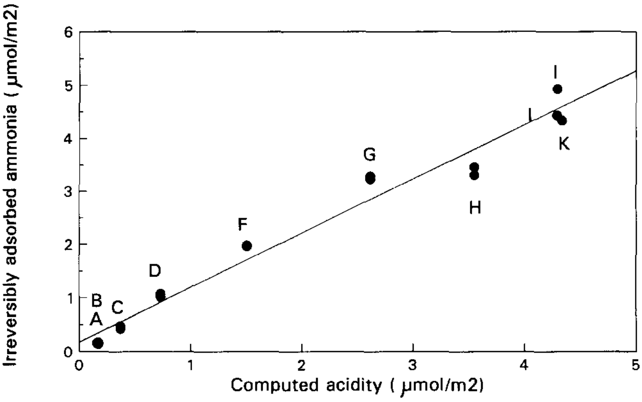

FIG. 8. Irreversibly adsorbed ammonia measured at 150°C versus calculated amount of ammonia assuming additivity of the acidities of SiO_2 and TiO_2. (●) Experimental points; (—) linear correlation.

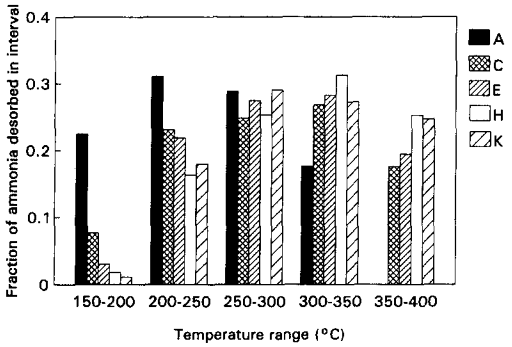

FIG. 9. The distribution of acid strength for the mixed oxides derived from the TPD curves from 150 to 400°C. The desorbed amounts were evaluated by integrating the TPD curve in 50°C intervals and they are normalized to the totally desorbed amounts of ammonia at 400°C for each material.

shifted slightly toward lower temperature (250–300°C). A varying portion of the ammonia is adsorbed on sites with such a high acidic strength that they are still covered when the temperature has reached 400°C. This is reflected in the low desorbed amounts for some of the oxides. With the equipment used it is not possible to examine changes in the acidic properties of the samples at very high acidic strength. However, in the area that can be investigated, no dramatic change can be seen in the acidic strength. One conclusion that can be drawn is that the amount of acid sites per unit surface area is increasing with increasing TiO_2 content. The change in acidic strength for sites that desorb ammonia below and up to 400°C obtained from the TPD profiles is small. The amount of acidic sites of the SiO_2–TiO_2 mixtures changes in a manner similar to that expected for the acidity of a mechanical mixture of two materials with different amounts of acidity.

TPD studies were also performed using the same GC coupled to a VG Pegasus SC mass spectrometer. The analysis of ammonia, water, nitrogen, nitric oxide, oxygen, argon, and nitrous oxide was performed simultaneously using the signals from masses 17, 18, 28, 30, 32, 40, and 44. The same pretreatment and experimental procedure as that for TPD on GC was applied for the mass spectrometer experiments. The results show that sample A (SiO_2) releases a large amount of water along with the ammonia during TPD. Taking into consideration the thermal conductivities of water and ammonia, the effect on the GC results can be simulated. Such an analysis shows that only the results for samples A and B are affected in significant ways. It can also be seen (Table 3) that the desorbed amount is only a few percent for samples A and B according to the GC results, while it is 60–80% for the other samples. This means that the conclusions drawn from the TPD results using GC hold for all samples except A and B. Thus there is no significant difference in the acidity strength distribution for oxides with TiO_2 contents of 10% and above. The estimation of the acidities of very strong sites will be dealt with in a separate article.

DISCUSSION

The results reported above can be interpreted according to the previous ones concerning the structural characterization of the same samples. We have in fact previously concluded that Ti enters in small amounts into the amorphous silica framework, as it does in crystalline silicalite (*27*) and in silica–titania glasses (*28*), assuming the relatively unusual tetrahedral coordination. This phase, which can be described as a substitutional solid solution of titania in silica, is the predominant phase in the silica–titania samples, where silica is the major component. Instead, we have concluded that silica tends to cover the anatase phase, producing a layer supported on it. Hence, titania-supported silica is also present and predominates in samples with high titania content.

From our data it is confirmed that Lewis acidity is absent on pure silica after usual activation procedures, as is well known. In fact, due to the covalency of this oxide, the condensation of surface hydroxy groups giving water and coordinatively unsaturated cations is difficult. Thus silica presents Lewis acidity only when evacuated under very severe conditions, as reported by Morrow and Cody (*29*).

Ti-containing samples, where silica predominates, show the presence of at least two types of Lewis sites. Very strong Lewis sites, which are absent on both pure silica and on pure titania, have been clearly shown both by CO and pivalonitrile adsorption. They have been identified as Ti^{4+} ions exposed on the surface and as having an incomplete tetrahedral coordination ($_3Ti^{4+}$). These sites are then considered to be related to the tetrahedral coordination taken by Ti^{4+} when it enters the silica framework. We can note that these sites have not been detected (possibly due to their low amount) on the surface of Ti-silicate, where tetrahedral Ti^{4+} is thought to be present and to act as the activation center for hydrogen peroxide in the catalysis of cyclohexanone ammoximation and related reactions (*30*). These sites are present neither on rutile TiO_2 nor on anatase (*19, 20*), because Ti^{4+} in these compounds takes an octahedral coordination. Thus, as far as the strength of Lewis sites is concerned, the samples containing 20–50% of titania are expected to be the most acidic in the Si–Ti–O series, and, as discussed above, they appear to be among the strongest solid acids known. This indeed agrees with literature data, which show silica–titanias to be extremely strong solid acids (*2, 6, 9*). In particular, Ko *et al.* (*9*) concluded by titration experiments performed on a series of silica—titanias that stronger sites are present on powders having a Ti : Si ratio of 25 : 75 than on the 50 : 50 and 75 : 25 ones, in agreement with our results.

These very strong Lewis sites are observed together with other sites that are similar to those normally found on both rutile (*20, 31*) and anatase (*19, 20*), identified as Ti^{4+} ions having a single coordinative unsaturation ($_5Ti^{4+}$) with respect to the overall coordination of six in the bulk. By increasing the amount of titania, the number of these sites certainly increase. However, the anatase phase in our silica–titania samples appears to be partially covered by a silica layer. This layer appears to cover the stronger Lewis sites of anatase, identified as Ti^{4+} ions having more than one coordinative unsaturation ($_4Ti^{4+}$) with respect to the overall coordination of six in the bulk and thought to be placed on edges and corners. Instead the more abundant Lewis sites of anatase ($_5Ti^{4+}$) are still well detectable. This effect has also been observed when anatase is impregnated with other metal oxides having anhydridic nature, such as V_2O_5, WO_3, and MoO_3 and with acids such as sulfuric and phosphoric acids (*32*). From this point of view SiO_2 behaves as the previously cited acidic supported phases with respect to anatase as a support.

The number of very strong Lewis sites ($_3Ti^{4+}$) is probably very small, in accordance with the very small solubility of Ti^{4+} in the silica framework. Their amount in absolute terms on the Si–Ti–O powders is expected to decrease along with the decrease of the amount of silica. As far as the amount of Lewis sites is concerned, the role of these strongest sites is probably negligible with respect to those present on the surface of anatase ($_4Ti^{4+}$ and $_5Ti^{4+}$) and of silica-covered anatase ($_5Ti^{4+}$). Hence, the number of Lewis sites is expected to increase in relation to the increasing amount of the TiO_2 component. This is exactly what is observed in our ammonia adsorption experiments, considering the irreversibly adsorbed species, thought to be entirely due to Lewis-bonded ammonia.

The above results indicate also that the samples in which silica is predominant show only a very small increase of the Brønsted acidity of surface silanol groups with respect to silica. Addition of silica to titania also causes an increase of Brønsted acidity, because silanols are more acidic than TiOH groups (*19*). In any case all silica–titanias remain substantially weak Brønsted acid solids, being unable to protonate not only a relatively weak base such as pyridine, but also stronger bases such as ammonia and *n*-butylamine. From the point of view of the Brønsted acid strength our data indicate that silica–titanias are significantly weaker than titanias doped by sulfate, phosphate, tungstate, and molybdate ions (*32, 33*), as well as of sulfated and phosphated silica (*33, 34*). The high acidity of silica–titanias reported by several authors (*6–9*) can therefore be attributed mostly to their Lewis acid strength. In this respect we can also cite the recent data of Kataoka and Dumesic (*35*), who found that titania-on-silica is also a Lewis acid, without a significant Brønsted acidity.

The mixed oxides characterized in this paper were prepared by precipitation using aqueous solutions of Na_2SiO_3. It is possible that a silica sol is formed when the basic solution is made acidic by the addition of HCl. Indeed, we have reported (*14*) that small (1.1 nm) entities of a microcrystalline cristobalite are present in the samples with high silica contents. During the precipitation procedure, the silica and titania could thus be obtained in separate phases as well as in mixed oxides. This could explain the experimental results showing additivity of acidities. Ko *et al.* (*9*) prepared SiO_2–TiO_2 mixed oxides from $TiCl_3$ and $SiCl_4$ in MeOH by addition of NH_4OH. After calcination for 2 h at 500°C the acidity was determined by the Benesi method. Acidities, at $pK_a + 3.3$, varied from 0 in pure SiO_2 over a maximum of 5.92 μmol/m^2 for 25 wt% TiO_2 to 2.44 μmol/m^2 for 100% TiO_2. Using Hammett indicators, the 25% TiO_2 sample was shown to contain the strongest acid sites (pK_a -8.2). This is similar to our results showing the highest acidic strength in the 10% TiO_2 sample. Only the oxide with 100% TiO_2 contained any anatase as detected by XRD. This is at variance with our results showing the presence of anatase in all samples containing TiO_2. Tanabe *et al.* (*39*) prepared a TiO_2–SiO_2 mixed oxide with 90 mol% TiO_2 by a homogeneous and by a heterogeneous method from $(C_2H_5)_4SiO_4$ and $TiCl_4$. The same homogeneous method that we used produces a material with a lower acidic strength than the heterogeneous one having no acidic sites of $H_0 \leq -3.0$. However, the amount of the acidic sites is larger on the homogeneously precipitated material. The amount was 2.3 and 4.6 μmol/m^2 at $H_0 = 3.0$ for the two methods. The latter value agrees neatly with ours, around 4.4 μmol/m^2 at 90 mol% TiO_2 (sample H). Itoh *et al.* (*37*) prepared mixed oxides by coprecipitation of mixed solutions of ethyl orthosilicate and titanium tetrachloride with ammonia. The acidity was measured by titration with *n*-butylamine in benzene and by adsorption of basic molecules from the gas phase. The specific acidity, at $H_0 \leq 1.5$, was strongly dependent on the calcination temperature. At 500°C, acidities of 0.8, 1.9, and 1.7 μmol/m^2 were obtained for 10, 50, and 90 mol% TiO_2 with a maximal acidity in the 50% sample. When the calcination was performed at 650°C, no such maximum was obtained. The adsorption of NH_3 from the gas phase studied, using a microbalance, yielded a value of 0.54 mmol/g for a 50% TiO_2 oxide at 150°C. This is close to the amount of irreversibly bound ammonia determined by us to 0.46 mmol/g. Thus the starting material has a large effect on the formation of acid sites in mixed oxides. When sodium silicate is used, the specific acidities of the mixed oxides behave largely as would be expected for a mechanical mixture of SiO_2 and TiO_2. There is a linear relationship, with a slope of 1, between the experimental values and the calculated values for a mechanical mixture. Very strong acid sites have been detected by IR. These sites are included in the acidities measured by ammonia adsorption using the GC method, but since the irreversibly bound ammonia increases linearly with the TiO_2 content their amount must be small.

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