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Study of the surface acidity of TiO_2/SiO_2 catalysts by means of FTIR measurements of CO and NH_3 adsorption

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Abstract

Samples were prepared by grafting different amounts of titanium isopropoxide ($Ti(O–Pr^i)_4$) onto silica surface in N_2 atmosphere, followed by steam hydrolysis and calcination. Either dioxane or toluene was used as a solvent. The surface properties of TiO_2/SiO_2 catalysts were studied by means of FTIR spectroscopy of adsorbed probe molecules, CO, and ammonia. Adsorption of CO at nominal 77 K exhibited different surface sites: (i) two families of Ti^{4+} cations, namely associated and isolated sites, with bands in the 2183–2194 and 2173–2177 cm^{-1} ranges respectively, shifting with coverage; (ii) surface Si–OH groups; and (iii) at titanium loadings >8 wt% TiO_2, corresponding to the alkoxide monolayer coverage of silica, TiOH species exhibiting an acidity higher than expected (observed shift $\Delta\nu = 200\ cm^{-1}$), probably due to interaction with the support. With increasing the titanium loading, the band at 2176 cm^{-1} disappears, indicating that associated Ti^{4+} sites form at the expense of isolated ones. Adsorption of ammonia at room temperature confirms the data obtained with CO. The use of apolar solvents seems to cause anchoring of the Ti alkoxide on the dehydrated portions of the silica surface, with consequences for the final state of the catalyst. In agreement with this observation, activity was lower for catalysts prepared in toluene than in those prepared using dioxane. Prepared catalysts were rather effective in the transesterification of refined oils with methanol.

Keywords: FTIR spectroscopy; CO; NH_3; TiO_2/SiO_2; Grafting

1. Introduction

In the last few years, the synthesis of well-dispersed supported transition metal oxides for use as supports and catalysts has attracted growing interest [1]. An interesting example is that of titania supported on silica catalysts (TiO_2/SiO_2), which has been considered as an advanced support materials as substitutes for pure TiO_2. The higher mechanical strength, thermal stability, and specific surface area of supported titania oxides compared with pure TiO_2 have attracted much attention and driven the interest in using these materials not only as catalytic supports, but also as catalysts themselves [2–4] for a wide variety of reactions, including selective oxidation [5] and epoxidation of olefins with alkyl hydroperoxide [6], isomerization [7], dehydration [8], and transesterification [9–11].

Several preparation methods have been used, including impregnation, chemical vapor deposition (CVD), atomic layer deposition (ALD), and liquid-phase grafting. These preparation routes often involve a highly reactive precursor, such as $TiCl_4$ or a Ti-alkoxide, to react with the hydroxyl groups of silica [9]. The reaction of surface hydroxyls with Ti precursors can be either monofunctional (i.e., one Ti-alkoxide molecule per OH group) or bifunctional (i.e., one Ti-alkoxide molecule titrating two OH groups) depending on: reaction temperature, alkoxide concentration, surface hydroxyl concentration, solvent used, and size and reactivity of the precursors [12,13]. Depending on the conditions, different types of Ti species may be present at the surface of silica when the Ti content is increased, ranging

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Table 1
Details concerning the operative conditions used for the preparation of the TiO_2/SiO_2 catalysts and some relevant physico-chemical and catalytic properties

Catalysts	$Ti(O–Pr^i)_4$ (g)	Support (g)	Volume of solvent (cm^3)	Grafting steps	Anchored metal (mmol Ti/g SiO_2)	wt% TiO_2	S_{BET} (m^2/g)	Y_{FAME} (%)
SiO_2	–	–	–	–	–	–	282	2.8
3.1TS-D	0.38	3.2	50	1	0.39	3.09	284	64.0
7.3TS-D	1.04	3.3	50	1	0.91	7.29	280	64.1
17.8TS-D	1.04	3.0	50	3	2.23	17.80	278	49.0
7TS-Tol	1.04	4.0	200	1	0.87	7.00	268	47.6
18TS-Tol	9.26	23.7	200	3	2.25	18	274	44.4
TiO_2	–	–	–	–	–	100	80	2.7

from highly dispersed TiO_x species at low titanium coverage to polymeric TiO_x species up to TiO_2 crystallites.

Previous work, concerning the catalytic performance of TiO_2/SiO_2 catalysts in both the transesterification of vegetables oils with methanol [11] and the epoxidation of cyclo-ctene with cumene hydroperoxide [14], has suggested that the surface titanium dispersion and the surface structure of the Ti sites are important activity-determining factors, because in both of these reactions, an increase in activity was observed with increasing TiO_2 loading up to the surface monolayer coating, followed by a decrease when larger amounts of TiO_2 were deposited. Ammonia TPD measurements have been used to study acidic sites from a quantitative point of view [11]. Results obtained are in agreement with the results of pyridine and dimethylpyridine TPD [19]. According to this paper, the number of Lewis acid site increases with increasing amounts of titania grafted on silica, until about a monolayer coating is reached, after which a decrease in the amount of TiO_2 occurs exceeding the monolayer obtained by repeating the grafting operation; this is due to the decreased TiO_2 dispersion.

Structural features of supported TiO_2/SiO_2 oxides and their relationship with the physicochemical and catalytic properties remain poorly understood due to the lack of systematic fundamental studies as abound for anatase phases [15–18]. To study the nature and abundance of Ti^{x+} and hydroxyl sites at the surface of TiO_2/SiO_2 systems, with different Ti loadings, we monitored CO adsorption at nominal 77 K and NH_3 adsorption at room temperature by means of FTIR spectroscopy.

2. Experimental

2.1. Preparation of catalysts

A commercial silica (Grace S432, specific surface area = 320 m^2/g; pore volume = 1.02 cm^3/g; hydroxyl density = 0.92 mmol/g) was used as support after calcination in air at 773 K for 8 h. The grafting method adopted for the preparation of TiO_2/SiO_2 catalysts using dioxane as a solvent was similar to that described elsewhere [20].

A different procedure was used for catalysts prepared in toluene as a solvent. In this case, the reaction was performed in a jacketed glass reactor of 200 cm^3 for 6 h under stirring at the boiling temperature of toluene (388 K). The solid was filtered off, washed with toluene, dried at 393 K overnight, hydrolyzed with steam, and finally calcined at 773 K for 2 h. In all cases, the amount of adsorbed titanium was determined using the colorimetric method of Snell and Ettre [21], by evaluating the quantity of titanium remaining in solution after the grafting reaction.

Table 1 presents the operative conditions adopted during the synthesis, along with the samples' BET surface areas. The catalysts are referred to as XTS-D/Tol, where X is the percentage by weight of TiO_2 and T represents TiO_2, S represents SiO_2, D represents dioxane, and Tol represents toluene. Previous work [20] showed that about 8 wt% of TiO_2 (~1 mmol Ti/g SiO_2) corresponds to the nominal surface monolayer coverage of silica by titanium tetra-isopropoxide; the hydroxyl group's concentration of the silica support (Grace S-432) is 0.92 mmol OH/g SiO_2.

2.2. Characterization techniques

Textural analyses were carried out using a Thermoquest Sorptomatic 1990 instrument (Fisons Instruments) and determining the nitrogen adsorption/desorption isotherms at 77 K. The samples were thermally pretreated under vacuum overnight up to 473 K (heating rate = 1 K/min). Specific surface area and pore distributions were determined using the BET and Dollimore–Heal methods [22,23].

For FTIR measurements, powder samples were pressed into thin, self-supporting wafers. Spectra were collected at a resolution of 2 cm^{-1} on a Bruker FTIR Equinox 55 spectrophotometer equipped with an MCT detector. Pretreatments were carried out using a standard vacuum frame in an IR cell equipped with KBr windows. To remove water and other atmospheric contaminants, wafers were outgassed for 1 h at 723 K before adsorption of CO at nominal 77 K and of NH_3 at room temperature.

Because of the weakness of the interaction with CO, adsorption was studied at low temperatures. Spectra were recorded at the nominal temperature of liquid nitrogen, by dosing increasing amounts of CO (in the 0.05–15 mbar equilibrium pressures range) on samples previously outgassed at 723 K inside a special quartz IR cell, allowing simultaneous dosing of carbon monoxide and addition of liquid N_2. After each experiment, an evacuation step was performed, to study the reversibility of the interaction.

Because it interacts more strongly with ammonia than with CO, NH_3 was dosed at room temperature in the equilibrium pressure range 1.00×10^{-2}–17.0 mbar, after which the reversible fraction of the adsorbate was removed through prolonged evacuation.

2.3. Catalytic tests

The catalytic screening was performed in small stainless steel vial reactors. The reaction was carried out by introducing reagents (0.9 g of methanol and 2.0 g of soybean oil) and a weighed amount (0.1 g) of catalyst into each reactor. The reactors were then heated in a ventilated oven, under constant agitation. The oven temperature was kept at 50 °C for 14 min, then increased at a rate of 20 °C/min up to 180 °C. After 1 h, the temperature was quickly decreased by immersing the vials in a cold bath.

The fatty acid methyl ester (FAME) yields were determined using the H-NMR technique [24] (Bruker 200 MHz), by measuring the ratio of the H-NMR signals related to the methoxylic (A_1) and methylenic groups (A_2), respectively:

$$Y_{\mathrm{FAME}} = \frac{A_1/3}{A_2/2}.$$

3. Results and discussion

3.1. Hydroxyls spectra of samples outgassed at 723 K

Fig. 1 reports spectra of all samples outgassed at 723 K in the OH stretch region (3800–3400 cm^{-1}), normalized to unit weight to allow comparison. It also gives a spectrum of the commercial silica (Grace S-432) used as support. All spectra exhibit a prominent band at about 3745 cm^{-1} due to isolated silanols, invariably observed at the surface of dehydrated silicas.

With pure silica (curve 1), a component is seen at 3742 cm^{-1} (arrow), assigned to isolated/geminal silanol couples [25], as depicted in Scheme 1. The spectrum also shows a tail on the low-frequency side, due to some heterogeneity of sites, as expected for silicas outgassed at 723 K.

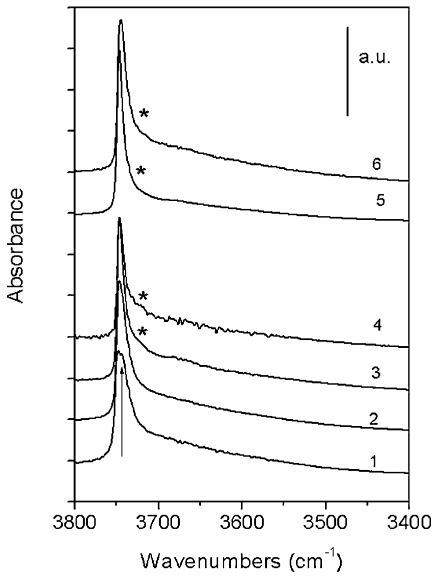


Fig. 1. FTIR spectra of samples outgassed at 723 K, in the 3800–3200 cm^{-1} range. Spectra normalized to samples unit area, in order to allow comparison, are reported of samples: Grace S-432 (curve 1); 3.1TS-D (curve 2); 7.3TS-D (curve 3): 17.8TS-D (curve 4); 7TS-Tol (curve 5); 18TS-Tol (curve 6).

When Ti is present, the component at 3742 cm^{-1} decreases in intensity (starting with sample 3.1TS-D, curve 2), and disappears at higher Ti loadings; with sample (curve 3), corresponding to a nominal monolayer coverage, only the band of free silanols is seen, and its intensity does not change much even at higher Ti loadings. The disappearance of the 3742 cm^{-1} band is probably related to the slightly more acidic nature of the species in Scheme 1 compared with the free silanols.

The constant intensity of the band at 3745 cm^{-1} strongly suggests that under the experimental conditions adopted here, grafting with alkoxysilanes occurs preferentially onto silanol-free surface patches (e.g., reactive siloxanes bridges) rather than on isolated silanols. This is in agreement with results of Brunel et al. [26], who reported a similar conclusion for the grafting of triethoxymethylaminopropane.

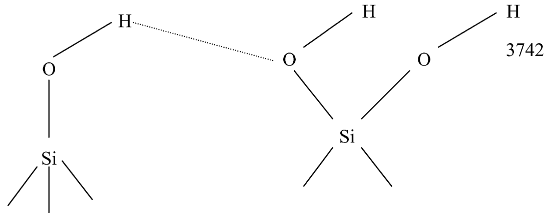
At high titanium loadings (curves 3–6), a new component appears at 3720 cm^{-1} (denoted by *), assigned to new Ti–OH species. As the intensity of silanols band at 3745 cm^{-1} is weakly affected by titanium loading, such new species likely will not be formed at the expense of silanols, but will grow onto the grafted phase.

3.2. Adsorption of CO at nominal 77 K on TiO_2/SiO_2 systems

Carbon monoxide is widely used as a probe molecule to detect the presence and the nature of Lewis acidic sites as well as Brønsted sites (in the present case acidic hydroxyls), to which it may H-bond. When the interaction between CO and the adsorbing site has basically an electrostatic nature (as in the foregoing cases), a hypsochromic shift occurs with respect to the free CO molecule (2143 cm^{-1}) [27].

Figs. 2–7 report difference spectra obtained after subtracting those of the bare samples depicted in Fig. 1. Two spectral ranges are considered: that of the hydroxyl stretch mode [ν(OH), 3800–3400 cm^{-1}; sections a of the figures] and that of the C≡O stretch mode [ν(CO), 2250–2050 cm^{-1}; sections b of the figures].

Fig. 2 reports spectra normalized to unit weight obtained after CO dosage on sample 3.1TS-D. With increasing CO pressure, a negative band develops at 3744 cm^{-1}, whereas a broad adsorption forms centered at 3666 cm^{-1} and with a shoulder at ca. 3600 cm^{-1}. These features are due to H-bonding among CO molecules and OH species; those originally absorbing at 3745 cm^{-1} (isolated silanols) shift to 3666 cm^{-1} ($\Delta\nu = 79\ \mathrm{cm}^{-1}$), as do silanols at the surface of dehydroxylated silicas ($\Delta\nu = 80\ \mathrm{cm}^{-1}$), indicating that the acidity of silanols is not altered by the presence of titanium. The shoulder



Scheme 1.

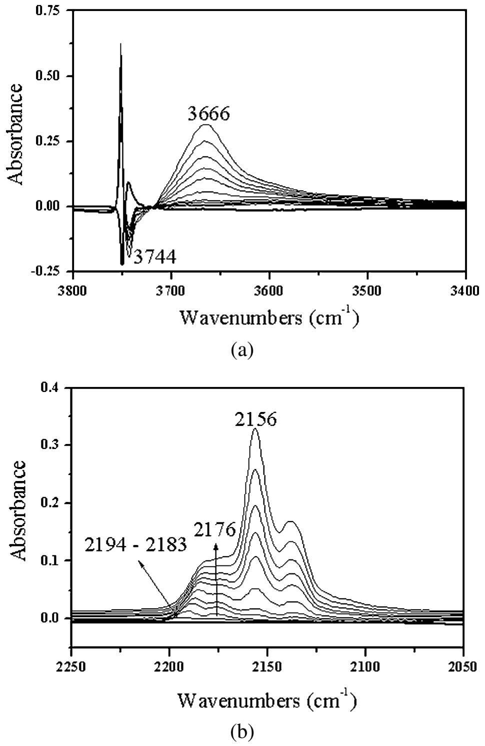


Fig. 2. FTIR difference spectra of CO adsorbed at nominal 77 K on sample 3.1TS-D, in the hydroxyls stretch range (a) and in the CO stretch range (b). Normalized spectra are reported, recorded under the following equilibrium pressures, from top to bottom: 25.0; 19.3; 6.8; 4.6; 2.9; 1.1; 0.50; 0.30; 0.21; 0.14; 0.098 mbar.

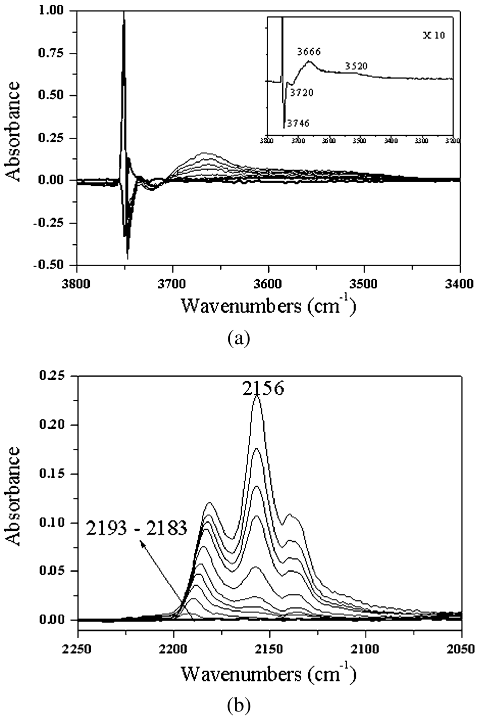


Fig. 3. FTIR difference spectra of CO adsorbed at nominal 77 K on sample 7.3TS-D, in the hydroxyls stretch range (a) and in the CO stretch range (b). Normalized spectra are reported, recorded under the following equilibrium pressures, from top to bottom: 25.0; 13.4; 9.3; 6.1, 4.0; 2.6; 1.6; 1.0; 0.86; 0.39; 0.083 mbar.

at 3600 cm^{-1} is due to more acidic silanols, visible in the spectrum of the bare sample (curve 2 in Fig. 1) as a tail to the band at 3745 cm^{-1}. The interaction with hydroxyls is reversible; the original IR spectrum was recovered after prolonged evacuation. The positive peak observed is due to slight changes in temperature caused by the gas phase.

The band at 2156 cm^{-1} (Fig. 2b) is due to the CO stretch mode of carbon monoxide molecules interacting via H bonding with silanols. It develops only at higher CO equilibrium pressures, being a weaker interaction compared with those at other acidic sites; the signal at ca. 2138 cm^{-1} is due to physisorbed CO.

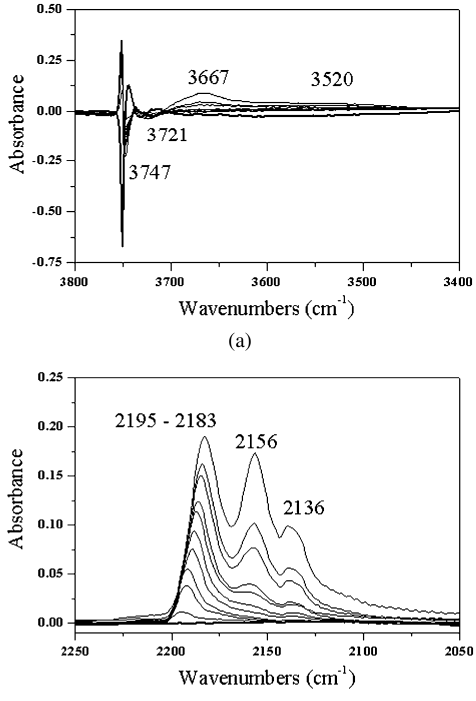
At higher wavenumbers, bands are seen at 2194 cm^{-1}, shifting to 2183 cm^{-1} with coverage, and at 2176 cm^{-1}. With bulk TiO_2 (anatase), CO adsorption gives rise to well-separated bands at 2205 and 2189 cm^{-1} [28], due to the presence of two families of coordinatively unsaturated Ti^{4+} ions, but different acidic sites are expected with TiO_2 supported on SiO_2. According to Hadjiivanov et al. [29], bands at 2194 and 2176 cm^{-1} are assigned to associated and isolated Ti^{4+} sites, respectively, both of which adsorb CO in a reversible manner.

The shift of the former band from 2194 to 2183 cm^{-1} is considered due to the collective behavior of CO oscillators adsorbed on associated Ti^{4+} sites of an extended phase. This is because the shift is relatively large compared with that of other oxide systems, meaning that adsorption sites cannot be considered isolated Ti^{4+} cations. According to Hadjiivanov et al. [29,30], these sites can be assigned to titanium cations having at least one coordinatively unsaturated Ti^{4+} cation in the second coordination sphere.

Hadjiivanov and co-workers have shown, by means of adsorption experiments of ^{12}CO–^{13}CO mixtures, that both static and dynamic contributions affect the $\nu(CO)$ shift [30]. The dynamic interaction brings about a blue shift, whereas the static interaction lowers the CO frequency.

For the second type of site, the static shift is very small, suggesting that these sites represent isolated titanium cations. This is consistent with the small static shift for CO adsorbed on titania–silica systems with low concentrations of titanium cations [31,32].

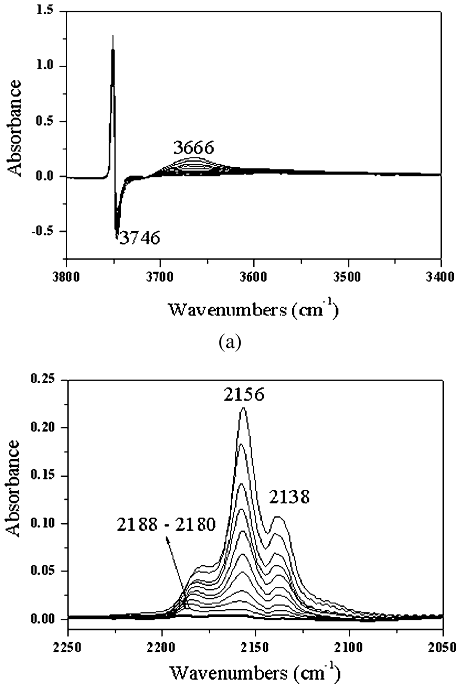
Figs. 3a and 3b report difference spectra obtained with sample 7.3TS-D. In the $\nu(OH)$ region (Fig. 3a), along with the band of isolated silanols shifting from 3746 to 3666 cm^{-1} due to the formation of H-bonding, new species are seen: a band at 3720 cm^{-1}, shifting to 3520 cm^{-1}, that is absent in sample 3.1TS-D, which has a lower Ti loading. Such a feature is better observed in the inset to Fig. 3a, which reports the last spectrum magnified by a factor of 10. The band at 3720 cm^{-1} may be due to the presence of another kind of hydroxyl group, nonsilica hydroxyls, with higher acid strength than free silanols. The observed shift of 3720 to 3520 cm^{-1} (200 cm^{-1}) is larger than that of TiOH groups at the surface of pure TiO_2 [33], meaning that more acidic TiOH species occur, probably due to a synergic effect of the silica support. The corresponding CO stretch mode (Fig. 3b), expected at about 2165 cm^{-1}, being of low intensity, is probably masked by the other two prominent bands at 2193–2183 cm^{-1} and 2156 cm^{-1} (Fig. 3b).



(a)

(b)

Fig. 4. FTIR difference spectra of CO adsorbed at nominal 77 K on sample 17.8TS-D, in the hydroxyls stretch range (a) and in the CO stretch range (b). Normalized spectra are reported, recorded in the 0.05–15 mbar equilibrium pressures range. Normalized spectra are reported, recorded under the following equilibrium pressures, from top to bottom: 19.9; 12.2; 8.2; 5.7; 3.8; 2.4; 1.3; 0.7; 0.3; 0.18; 0.089 mbar.



(a)

(b)

Fig. 5. FTIR difference spectra of CO adsorbed at nominal 77 K on sample 7TS-Tol, in the hydroxyls stretch range (a) and in the CO stretch range (b). Normalized spectra are reported, recorded under the following equilibrium pressures, from top to bottom: 19.3; 11.9; 8.5; 5.8; 4.1; 2.5; 1.7; 1.0; 0.5; 0.1; 0.089 mbar.

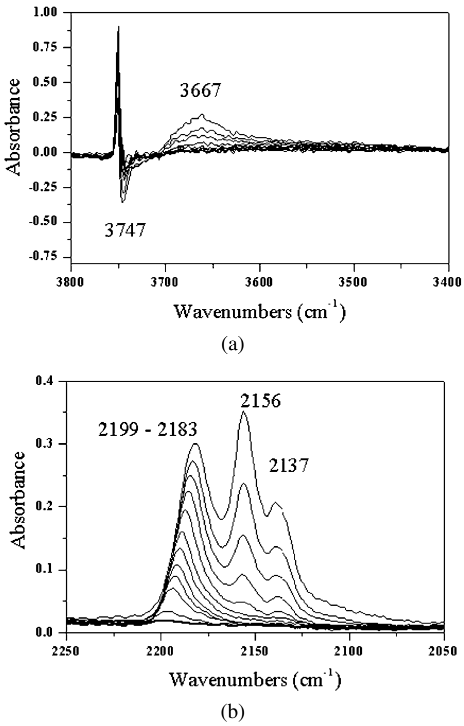
The band at 2193–2183 cm^{-1}, as discussed before, is assigned to CO molecules interacting with "associated" Ti^{4+} sites [27], and that at 2156 cm^{-1} is assigned to CO interacting via H bonding with surface Si–OH groups. It is noteworthy that isolated Ti^{4+} sites should be absent in sample 7.3TS-D, because the corresponding band at 2176 cm^{-1} is not observed, and new Ti–OH species are formed.

With sample 17.8TS-D, the same species are observed in the O–H stretch region as for sample 7.3TS-D (Fig. 4a). The most relevant difference observed after CO dosage on sample 17.8TS-D is observed in the CO stretch range (Fig. 4b) with an increased intensity of the band at 2195–2183 cm^{-1}, due to CO on associated Ti^{4+} sites, compared with that of CO adsorbed on hydroxyls (2156 cm^{-1}). Such behavior indicates that the hydroxyl population remains more or less constant with increasing titanium loading, while an extended titania phase in which vicinal Ti^{4+} cations are present is formed. This semiquantitative evaluation is in agreement with previously reported findings [11,14,20], according to which, at low Ti loadings, species with titanium in tetrahedral coordination seem to be prevalent on the catalyst surface until the surface monolayer coating is reached ($\sim$2.2 Ti atoms/nm^2). In contrast, the degree of the polymerization of Ti species increases with further increase in TiO_2 loading, leading to a large number octahedral Ti sites grafted on SiO_2.

To illustrate the possible association between the solvent used during preparation and the surface properties of grafted TiO_2/SiO_2 catalysts, CO adsorption at nominal 77 K is reported in Fig. 5 for sample 7TS-Tol and in Fig. 6 for sample 18TS-T, obtained using toluene instead of dioxane. For sample 7TS-Tol, in the OH stretch range the band of isolated silanols at 3747 cm^{-1} is seen to shift to 3667 cm^{-1} on CO adsorption; in the CO stretch range, a band at 2188 cm^{-1} is seen to shift to 2180 cm^{-1} with coverage, and at high CO partial pressure, bands of CO adsorbed on isolated silanols (2156 cm^{-1}) and of physisorbed CO (2138 cm^{-1}) are seen (Fig. 5). With respect to sample 7.1TS-D, with comparable titanium loading, the main difference concerns the absence of TiOH species; the corresponding band at 3720 cm^{-1} is not seen.

Similar results are obtained for sample 18TS-Tol (Fig. 6); that is, only the band of isolated silanols (at 3800–3400 cm^{-1}) and that of associated Ti^{4+} sites (2199–2183 cm^{-1}), besides those at 2156 and 2138 cm^{-1} assigned above, are seen. The band associated with Ti^{4+} sites is observed at slightly higher wavenumbers (2199 vs 2195 cm^{-1}) with respect to sample 17.8TS-D with comparable titanium loading, indicating greater exposure of Ti^{4+} cations at the surface acting as stronger acidic Lewis sites compared with sample 17.8TS-D. Using toluene instead of dioxane as a solvent seems to favor formation of an extended TiO_x phase with highly uncoordinated Ti^{4+} cations with respect to the formation of TiOH species.

These characterization data demonstrate that the solvent used for dispersing the Ti alkoxide crucially affects the surface structure of the supported Ti species as well as the final surface dispersion. This is likely due to the formation of titanium alkoxide clusters of greater size in the apolar solvent, as well as to the greater affinity of these clusters for the polar surface with



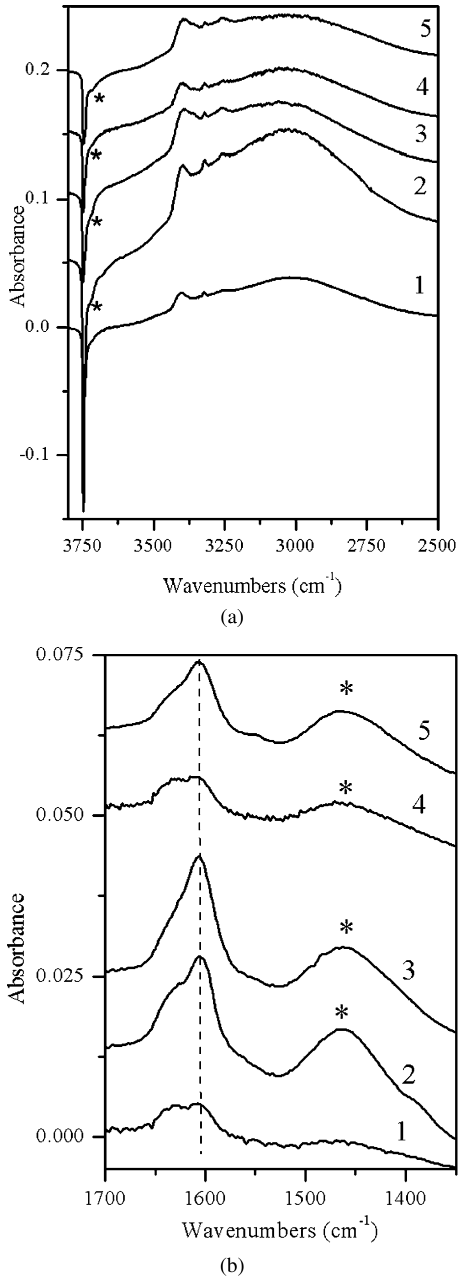
(a)

(b)

Fig. 6. FTIR difference spectra of CO adsorbed at nominal 77 K on sample 18TS-Tol, in the hydroxyls stretch range (a) and in the CO stretch range (b). Normalized spectra are reported, recorded under the following equilibrium pressures, from top to bottom: 20.4; 14.1; 9.80; 6.60; 4.4; 2.9; 1.7; 1.0; 0.5; 0.1; 0.052 mbar.

respect to the solvent, which favors the increased adsorption of titanium alkoxide on silica. The experimental findings are in agreement with previous results [11] obtained by XPS measurements done on TiO_2/SiO_2 samples prepared using dioxane and toluene as solvents. This investigation revealed that the catalysts prepared by performing the grafting reaction in toluene showed a lower I_{Ti}/I_{Si} intensity ratio than the corresponding catalysts prepared in dioxane, characterized by the same Ti/Si bulk atomic ratio.

The foregoing findings demonstrate that the surface properties of these TiO_2/SiO_2 systems differ significantly from those of pure oxides. Several studies have shown that CO adsorption on both anatase and rutile TiO_2 modifications results in the appearance of Ti^{4+} carbonyls that are clearly visible at ambient temperature [34,35]. Two Ti^{4+} sites have been reported at the surface of anatase, the maxima of the respective bands located at 2208 (α sites) and 2192 (β sites) cm^{-1}, at low coverage, shifting to 2206 and 2186 cm^{-1}, respectively, at high coverage [28,34]. In contrast, with the present TiO_2/SiO_2 catalysts, CO adsorption at ambient temperature was negligible, indicating that in general, the solids investigated are characterized by a weaker Lewis acidity that TiO_2 itself. Thus, the absence of strong Lewis acid sites on grafted TiO_2/SiO_2 catalysts is the main difference compared with pure titania. This is an important finding, significantly influencing the performance of TiO_2/SiO_2 catalysts with respect to TiO_2 itself, as reported below. In contrast, Lewis acidity appears to be similar to that of other silica-supported titania catalysts [31] and of titanium silicalite [33,36].



(a)

(b)

Fig. 7. FTIR difference spectra recorded after dosing at room temperature ca. 5 mbar of NH_3 on samples outgassed at 723 K. (a) OH stretch region (3800–2500 cm^{-1}); (b) N–H bending region. Curve 1: sample 3.1TS-D ($p_{NH_3} = 4.6$ mbar); curve 2: sample 7.3TS-D ($p_{NH_3} = 4.7$ mbar); curve 3: sample 17.8TS-D ($p_{NH_3} = 4.6$ mbar); curve 4: sample 7TS-Tol ($p_{NH_3} =$ 4.1 mbar); curve 5: sample 18TS-Tol ($p_{NH_3} = 5.1$ mbar).

3.3. Adsorption of NH_3 at room temperature on TiO_2/SiO_2 systems

Ammonia is probably the most frequently used probe molecule for acidity assessment, because it can interact with both Brønsted acidic sites (by forming ammonium ions) and Lewis acidic sites (by forming acidic–basic adducts) [37]. Its small size allows quantitatively probing of almost all acid sites in micro-, meso-, and macro-porous oxides [38]. The protonated species (ammonium ions) and the coordinatively bonded ammonia differ, from a spectroscopic standpoint, in terms of NH deformations and stretching vibrations. The ammonium ion shows typical absorptions at 1450 and 3300 cm^{-1}, whereas co-ordinatively bonded ammonia molecules absorb at 1250, 1630, and ∼3330 cm^{-1}. In particular, the deformation vibrations (bending modes) at 1450 and 1630 cm^{-1} provide reliable indicators for the presence of protonated and coordinatively bonded ammonia, respectively.

Figs. 7a and 7b report normalized spectra taken after dosing about 5 mbar of ammonia on the five samples outgassed at 723 K. Spectra are reported after subtraction of the spectra of the bare samples, reported in Fig. 1. In the OH stretch range (Fig. 7a), a negative band at 3745 cm^{-1} and a broad absorption with a maximum at about 2990 cm^{-1} are seen in all samples. These features are readily assigned to the interaction of isolated silanols (3744 cm^{-1}) with ammonia molecules via the formation of H bonding. Because the interaction is much stronger than with CO, the observed shift is ca. 750 cm^{-1}, as is commonly observed with pure silica. Besides these features, another negative band is seen at about 3720 cm^{-1} in all samples except 3.1TS-D; in agreement with results of CO adsorption, this band is assigned to more acidic TiOH species.

Fig. 7b reports the same spectra in the NH bending mode region (1700–1350 cm^{-1}). For sample 3.1TS-D, a signal is seen at 1606 cm^{-1}, assigned to NH_3 molecules adsorbed on Ti^{4+} sites. The shoulder observed at ca. 1636 cm^{-1} is due to ammonia molecules interacting with isolated silanols via H-bonding. Such a band, seen only at appreciable ammonia pressure, is reversible on evacuation at room temperature (spectra not shown). With increasing titanium loading on samples synthesised in dioxane (curves 2 and 3), the intensity of the band at 1606 cm^{-1} increases markedly, and a new band occurs at ca. 1460 cm^{-1}. The latter feature is assigned to the formation of ammonium ions, due to the interaction of ammonia with more acidic TiOH species, absorbing at 3720 cm^{-1} in the original spectra. This conclusion is supported by the presence of a negative band in the OH stretching region (Fig. 7a, denoted by *). The interaction of ammonia with such TiOH species is only partially reversible after evacuation at room temperature (spectra not reported). No relevant differences were observed for the 7TS-Tol (curve 4) and 18TS-Tol (curve 5) catalysts, besides the fact that the contribution of more acidic TiOH species is lower with respect to samples with the same titanium content synthesized in dioxane.

3.4. Correlations between the surface properties and catalytic performances of grafted TiO_2/SiO_2 catalysts

It is well known that the catalytic performance of supported titanium oxide is significantly modified by interaction with the silica support, probably due to changes in the molecular structure and coordination environment. Previous work has characterized the catalytic behavior of TiO_2/SiO_2 catalysts prepared by grafting in the epoxidation reaction of cyclooctene with cumene hydroperoxide [14]. In the present work, the catalytic performance of transesterification of refined oil with methanol (on which biodiesel production is based) was studied on both TS-D (D: dioxane) and TS-Tol (Tol: toluene) catalysts.

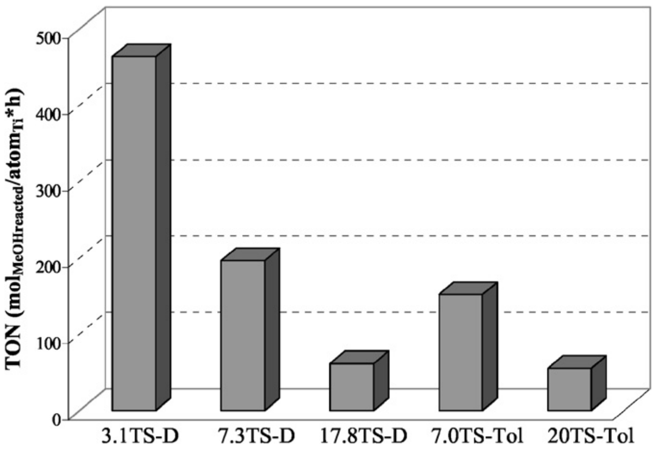


Fig. 8. Catalytic results expressed in terms of turnover number (TON), obtained in the transesterification reaction of refined oil with methanol for the series of TiO_2/SiO_2 prepared catalysts.

As demonstrated by the values related to the reactivity properties of the prepared catalysts, reported in the last column of Table 1, an increase of activity was observed with increasing TiO_2 loading until the surface monolayer coating was reached, followed by a decrease as more TiO_2 was deposited on the silica surface. It must be pointed out that catalysts containing 3–7 wt% of TiO_2 showed no difference in the observed activities. We have two different operating effects: (1) decreasing dispersion of TiO_2 with increasing grafted amounts and (2) formation of new sites. The two effects are contrasting, which explains why the activity does not change significantly in the range studied. For an amount of TiO_2 greater than a monolayer, the activity drops with a decrease in dispersion and the consequent disappearance of the Lewis sites of appropriate strength. The appearance of new, stronger Lewis sites observed on FTIR analysis for the less widely dispersed catalysts has no affect on catalytic activity. On the other hand, it is noteworthy that crystalline (anatase) TiO_2 showed no catalytic activity in the mentioned reaction. Our findings are in agreement with the results observed with homogeneous catalysts [39], which suggest that an optimal range of strength for Lewis acidic sites exists, and that very strong Lewis acidic catalysts are less active in transesterification reactions. As matter of fact, the acidic sites must coordinate the reactant molecules to some degree, but not so much as to also cause release of the products.

A possible influence of the solvent used in the preparation was also demonstrated; lower activity was noted for the catalysts prepared in toluene compared with those prepared in dioxane. Thus, the catalytic tests performed on the transesterification reaction confirmed the influence of the solvent used on the final structure of the active Ti sites, as indicated by FTIR measurements of adsorbed CO. The lower dispersion of titanium on silica surface for the catalysts prepared using toluene as solvent results from the lower activities observed experimentally. As mentioned earlier, it is noteworthy that very low activity was obtained in the presence of pure TiO_2 (see Table 1).

The FTIR results can be used to establish interesting correlations between the electrophilic nature of supported Ti^{4+}

sites (e.g., the acid strength of titanium cations) and their catalytic performances. Indeed, it is possible to attribute the decrease in activity caused by grafting TiO_2 amounts greater than surface monolayer coverage to the disappearance of isolated Ti^{4+} sites on the catalyst surface. This finding is highlighted by the trend in turnover number (TON) values (TON = $\text{mol}_{\text{MeOHreacted}}/\text{atom}_{\text{Ti}}\,\text{h}$) values reported in Fig. 8, indicating that the presence of isolated Ti sites on the surface of sample 3.1TS-D is a key factor in the catalytic performance of TiO_2/SiO_2 catalysts in biodiesel production.

This effect appears to be more pronounced for samples 17.8TS-D and 18TS-Tol, whose FTIR normalized spectra of adsorbed CO show higher concentrations of "associated" Ti^{4+} sites with respect to the solids with smaller amounts of supported titania. Moreover, FTIR measurements of absorbed NH_3 show an increase in Brønsted acid sites on these catalysts, attributed to the increase of Ti–OH groups with respect to the silica support due to a grafting reaction of titanium isopropoxide. According to these characterizations, lower activity in the transesterification reaction is found for the aforementioned solids. Finally, the results obtained in this work allow us to attribute the best catalytic behavior of samples 3.1TS-D and 7.3TS-D in the transesterification reaction to the greater dispersion of titanium sites, confirmed by the band at 2176 cm^{-1}, assigned to CO adsorbed onto isolated Ti^{4+} sites.

4. Conclusions

Our results allow us to establish interesting correlations between the electrophilic nature of supported Ti^{4+} sites (e.g., the acid strength of titanium cations) and their catalytic performance in the transesterification reaction of refined oil with methanol. The main results obtained by FTIR spectroscopy of adsorbed CO and NH_3 on TiO_2/SiO_2 catalysts prepared by grafting can be synthesized as follows:

- The interaction between titania and silica in silica-supported titania catalysts occurs on supported Ti^{4+} sites, characterized by a weaker Lewis acidity than on pure TiO_2.
- Two kinds of Lewis acid sites, differing in the electrophilic properties of the respective Ti^{4+} cations, were detected: isolated Ti^{4+} sites (2177–2173 cm^{-1}) mainly at low Ti loadings and associated Ti^{4+} sites (2194–2183 cm^{-1}).
- Hydroxyl groups with higher acid strength with respect to Si–OH groups of SiO_2 and to Ti–OH groups of TiO_2 were observed at the surface of sample 7.29TS-D, as indicated by the shift of the band from 3721 to 3520 cm^{-1} in the FTIR spectrum of adsorbed CO (Fig. 3a). This was also confirmed by ammonia adsorption. In fact, the band at 1465 cm^{-1} (see Fig. 7a) increased in intensity in parallel with the appearance of the band at 3716 cm^{-1}.
- Finally, the catalytic tests of the prepared TiO_2/SiO_2 catalysts showed that isolated Ti^{4+} cations have sufficient Lewis acid strength to catalyze the transesterification of refined oil with methanol.

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