Evidence of correlation between electronic density and surface acidity of sulfated TiO_2

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Received 8 March 2001; accepted 2 July 2001

Correlation between the electronic structure and surface acidity of TiO_2–SO_4^{2-} with different SO_4^{2-} amounts has been investigated by means of NH_3-TPD, NH_3-FT-IR and XPS. With the increase of sulfate loadings, the shift of binding energies of O 1s in hydroxyl and Ti $2p_{2/3}$ increases and is proportional to total acidity. A linear relation is obtained between Ti 2p binding energy shift and Lewis acid sites, while the shift in O 1s binding energy is attributed both to the generation of NH_3 hydrogen bond and of Brønsted acid sites. Accordingly, the results obtained from XPS measurements provide evidence that the ammonia adsorption sites are attributed to the decrease of electron density of O 1s in hydroxyl (Brønsted type and H bonded) and Ti $2p_{2/3}$ (Lewis type) by inductive effect of the neighboring sulfate ion.

KEY WORDS: electronic density; surface acidity; sulfated TiO_2

1. Introduction

It is known that TiO_2 surface acidity is modified either by using different preparation methods or in the presence of surface impurities [1,2]. In particular, the addition of a small amount of sulfate ions leads to the generation of new strong acidity [3,4]. It has been reported that not only strong Brønsted acid sites but also Lewis acid sites are generated by the presence of sulfate impurities. So far, many results have been published with respect to the mechanism of the acidity generation and the type of sulfate [5–7].

However, compared with mixed metal oxides and zeolites [1,8], no detailed correlation between the modification of surface acidity and the electronic density was found in sulfated titanium. In fact, in the characterization of TiO_2–SO_4^{2-} by XPS, Chen and Yang reported no shift in binding energy between unsulfated and sulfated samples [9].

In the present report, we attempt to characterize the electronic density of TiO_2–SO_4^{2-} by a systematic XPS study as a function of sulfate loading. Furthermore, we also propose correlations with acid properties.

2. Experimental

2.1. Preparation of catalysts

$Ti(OH)_4$ was prepared by precipitation of a titanium tetrachloride solution. The precipitate obtained by adding 25 wt% ammonia solution was washed with hot distilled water until no chloride ion was detected and dried at 100 °C for 12 h, then calcined at 500 °C for 5 h.

To obtain the sulfated catalyst, H_2SO_4 was used as an initial precursor of sulfate in the catalyst preparation. Titanium hydroxide obtained through precipitation of $TiCl_4$ was dried at 100 °C for 24 h. The calculated H_2SO_4 solution (0.1 N) was added to the titanium hydroxide. The solids were then dried for 12 h at 100 °C and calcined for 5 h at 500 °C. The real loading amounts of sulfate after calcination were verified by ICP analysis. The surface area and sulfur loadings of samples are shown in table 1. The detailed characteristics of samples have been documented in a previous paper [5].

2.2. Characterization

X-ray photoelectron spectra were obtained with a Surface Science Instruments SSX-100 model 206 spectrometer with a monochromatised Al Kα source, operating at 10 kV and 12 mA. Samples were compressed in a small cup under a 5 kg/cm^2 pressure for 30 s and supported on a holding carousel. The positive charge, developed on the samples due to the photoejection process, was compensated by a charge neutralizer. A low energy flood gun whose energy was adjusted at 8 eV with a Ni grid placed 3 mm above the samples was used to control charging on the sample surface. The charge compensation stability as a function of time was con-

Table 1
Structure and textural data.

Weight loading (%SO_4^{2-})	BET surface area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (Å)	Detected phase (XRD)
0	40	0.06	61	Anatase
1.5	58	0.09	65	Anatase
3.0	84	0.14	68	Anatase
6.6	104	0.16	63	Anatase

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1011-372X/01/0900-0027$19.50/0

trolled by recording the C 1s line at the beginning and the end of the analysis of each sample. The residual pressure inside the analysis chamber was below 5×10^{-9} Torr. The binding energies of O 1s, Ti 2p and S 2p were referenced to the C 1s band at 284.8 eV.

Atomic concentration ratios were calculated by correcting the measured intensity ratios with the theoretical sensitivity factor.

An NH_3-TPD (temperature-programmed desorption) spectrum was obtained by monitoring the desorbed ammonia, after ammonia adsorption on the catalyst at 100 °C using pure ammonia, while increasing the temperature of the sample at a constant rate (10 °C/min) and maintaining the carrier gas at a flow rate of 60 cm^3 He/min. The outlet gas was passed through a 20 wt% H_3BO_3 solution in order to check the amount of NH_3.

FT-IR spectra were recorded using a Brucker FT 88 spectrometer. The samples were pressed into self-supporting discs, placed in an IR cell, and treated under vacuum (10^{-6} Torr) at 400 °C for 2 h. To obtain the spectra of NH_3 adsorbed on the surface, after cooling to room temperature, the samples were exposed to ammonia for 3 min. Then, spectra were recorded after evacuation (5×10^{-5} Torr) for 30 min.

3. Results and discussion

Figure 1 shows the variation of atomic % of the peaks around 169 and 532 eV with different sulfate loadings. The sulfate ion consists of one sulfur and four oxygen ions bonded to the central sulfur ion. In XPS, the central atom of sulfate, S(6+) is identified around 169 eV, while the oxygen bonded to the central atoms of sulfur is shown around 532 eV as a shoulder of a main peak around 530 eV due to the oxygen bonded to the Ti atoms [8]. The results obtained with the different sulfate loadings show that the atomic ratio of both peaks linearly increases with the increase of sulfate contents and the ratio of slope between sulfur(6+) and O(2−) is calculated to 3.5. In the case of the peak around 532 eV, the ordinate for pure TiO_2 has been attributed to the contribution of the oxygen in carboxylate and/or other oxygen-bonded carbon species [10]. Accordingly, it is evidenced that the loaded sulfuric acid in the preparation converts to the sulfate type during the calcination.

Figure 2 shows the binding energy of the sulfur and oxygen at 532 eV bonded to the sulfate. The results show that the binding energy of sulfur atoms is not affected by the sulfate contents. The shift of oxygen binding energy in pure TiO_2 could be explained by a single contribution through the oxygen in carboxylate and/or other oxygen-bonded carbon species. In other words, the peak shift in sulfated samples as compared with pure TiO_2, is due to the increased contribution of oxygen in sulfate. Thus, it can be suggested that the increase of sulfate contents does not modify the binding energy of oxygen-bonded sulfur atoms.

The binding energy of Ti and oxygen bonded to TiO_2 shifts to higher binding energy as shown in figure 3. In pure TiO_2, the peaks due to Ti $2p_{2/3}$ and O 1s corresponded to 458.6 and 529.9 eV, respectively. After sulfation, the binding energy of Ti $2p_{2/3}$ and O 1s bonded to TiO_2 at the 6.6 wt% TiO_2–SO_4^{2-} is 459.1 and 530.3 eV, which is higher than the

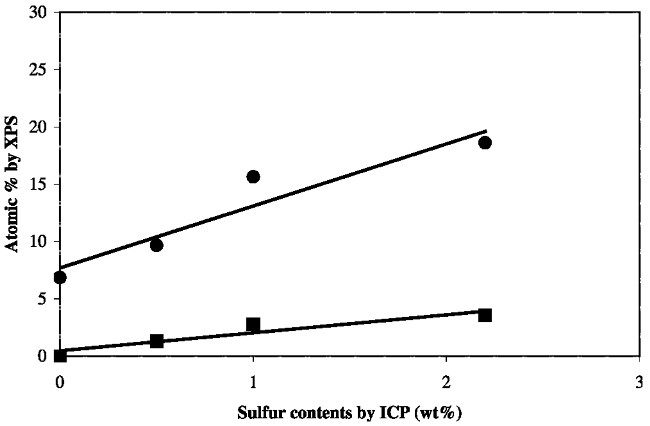

Figure 1. Variation of XPS atomic % of S 2p (■) and O 1s (•) in sulfate and carbon species as a function of sulfur contents measured by chemical analysis.

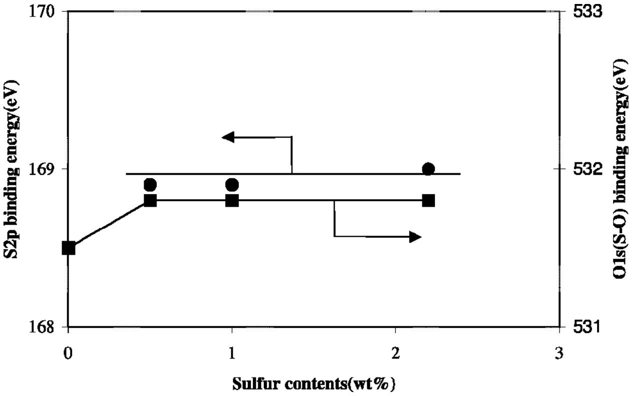

Figure 2. Correlation between the binding energy of S 2p and O 1s in sulfate and carbon species as a function of sulfate contents.

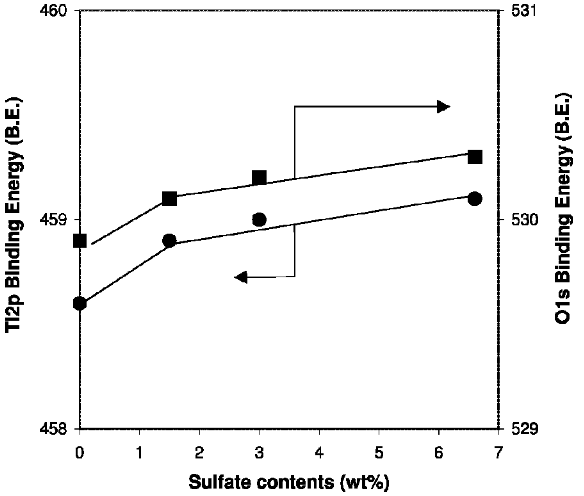

Figure 3. Correlation between the binding energy of Ti $2p_{2/3}$ and O 1s in bulk TiO_2 as a function of sulfate contents.

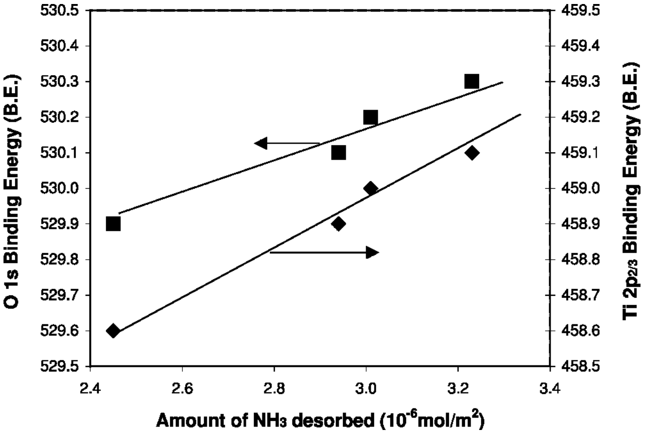

Figure 4. Correlation of the binding energy of Ti $2p_{2/3}$ and O 1s with acidity.

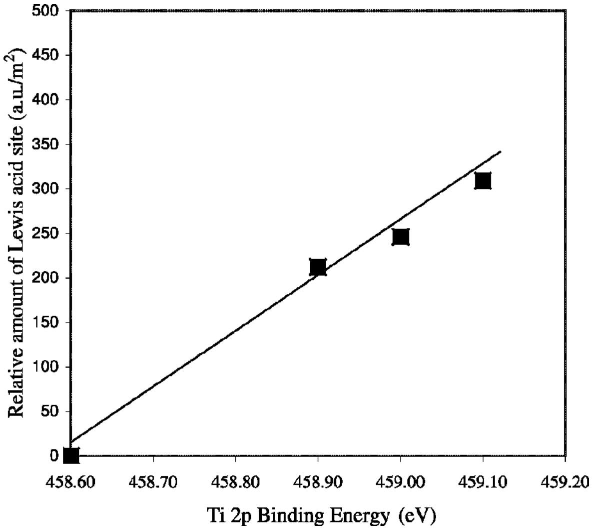

Figure 5. Correlation of the binding energy of Ti $2p_{2/3}$ with area of the peak at 1600 cm^{-1}.

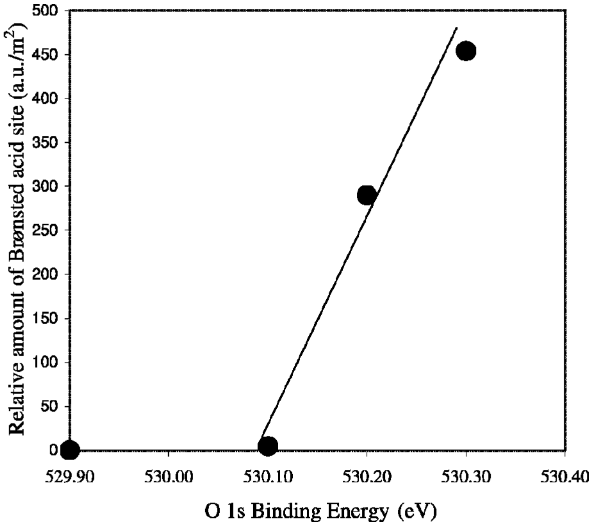

Figure 6. Correlation of the binding energy of O 1s with area of the peak at 1425 cm^{-1}.

value for unsulfated TiO_2. This upward shift of binding energy in XPS could be explained by the increase of effective positive charge. Accordingly, these results clearly suggest that the addition of sulfate ions on the surface TiO_2 causes a delocalization of electrons from bulk TiO_2. Furthermore, a linear relation between the binding energy and sulfate contents is also found in our samples. Since the differences in binding energies between the sulfated samples are very small and because of the error range in XPS, a repeated measurement was carried out. Thus, based on the difference between unsulfated and sulfated samples, we could propose that the sulfation of TiO_2 leads to the electron transfer from bulk TiO_2 to sulfate ions and causes the new distribution of electrons on the surface of TiO_2.

In order to elucidate the correlation between the charge redistribution due to sulfation and acid properties, total acidity and the distribution of Brønsted and Lewis acid sites were measured by NH_3-TPD and FT-IR. The NH_3 amounts measured in TPD experiment are normalized by surface area and the calculated values are correlated with the Ti 2p and O 1s binding energies obtained. As shown in figure 4, the amount of ammonia adsorbed on unit area is directly proportional to the upward shift of Ti 2p and O 1s binding energies. Based on these results, it is suggested that the upward shift of binding energy of TiO_2 in Ti and oxygen evidences the electron transfer to sulfate ions, and that the deficient electron in Ti and oxygen in the hydroxyl group on the TiO_2 surface becomes a driving force to generate acid sites, as suggested by Connell and Dumesic [11]. Especially, it can be proposed that Ti be responsible for Lewis acid sites, while Brønsted acid sites could be attributed to the OH on the TiO_2 surface.

In order to obtain the specific relation of the shift in Ti 2p and O 1s binding energy with Brønsted and Lewis acid sites, the FT-IR spectra were measured in all samples after evacuation at room temperature followed by ammonia adsorption. It is known that Lewis and Brønsted acid sites are assigned around 1425 and 1600 cm^{-1}, respectively. For comparison, the area of peaks observed at 1425 and 1600 cm^{-1} were integrated and were also normalized by surface area. Figures 5 and 6 show the relation between the normalized peak areas corresponding to Lewis and Brønsted acid sites and the Ti 2p and O 1s binding energies. As shown in figure 5, the increase of Ti 2p binding energy is proportional to that of the peak area observed at 1600 cm^{-1} assigned to Lewis acid sites. This correlation is in agreement with that of Ti 2p binding energy with total amount of ammonia. As shown in figure 6, the peak area at 1425 cm^{-1} obtained from 1.5 wt% TiO_2–SO_4^{2-} can be neglected as compared with 3.0 and 6.6 wt%, while the linear correlation between the shift in binding energy and the peak area at 1425 cm^{-1} appears in the sample with sulfate above 1.5 wt%. To explain this result, it should be considered that the ammonia adsorbed on OH bonds is attributed to hydrogen-bonded ammonia and the ammonia adsorbed on Brønsted acid sites. When the electron in O is not strongly attracted by a sulfate ion, hydrogen-bonded ammonia is mainly formed. It is known that this ammonia is very weakly attached to the surface and does not show any NH^{4+}

properties. Thus, the non-linear relation due to the negligible increase of Brønsted acid sites in 1.5 wt% TiO_2–SO_4^{2-} could be explained by the main formation of hydrogen-bonded ammonia. On the other hand, the linear relation shown in the samples with the higher sulfate contents indicates that the sulfate added over 1.5 wt% SO_4^{2-} fully contributed to the increase of Brønsted acid sites.

In summary, even though the generation of acidity in sulfated catalyst has been explained very well and is well-documented up to now, the electron evidence by XPS has not been fully documented yet, to our knowledge. Accordingly, these results provide new evidence to explain and confirm the model of the generation of acidity through the sulfation of metal oxide.

Acknowledgement

This work was supported by ECSC project (7220-ED/093). We also acknowledge the support of FNRS (Fonds National de la Recherche Scientifique, Belgium).

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