Reversible transformation between the isolated and the bidentately bound sulfate ion in sulfate promoted metal oxides

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A new experimental result of thermally treating ammonium sulfate–titanium oxide (AS–TiO_2) is reported. The results strongly suggest the reversibility of the transformation between the isolated and the bidentately bound sulfate ion involved in the sites responsible for the acidity and the catalytic activity of sulfate promoted metal oxides. On the basis of the results a scheme for the reversible transformation is suggested.

Keywords: Super acid; TiO_2; sulfate ion; IR; XPS

1. Introduction

It has been reported previously that by calcination at certain temperatures ammonium sulfate–metal oxides (AS–M_xO_y) or H_2SO_4–metal oxides can be converted into sulfate promoted metal oxides (SPMO), known as a new kind of solid super acid, such as SO_4^{-2}/ZrO_2, SO_4^{-2}/Fe_2O_3 and SO_4^{-2}/TiO_2 [1]. They are used for various acid-catalyzed reactions [2–4]. So far the real structure of the active sites responsible for the acidity and the catalytic activity is still an open question. All the previous results were obtained by studying AS–M_xO_y calcined at 773–973 K [1,5]. No reports, however, have been found concerning AS–M_xO_y treated below 773 K. Actually, the information from the investigation of AS–M_xO_y treated below 773 K is also valuable for understanding the structure of the active site in SPMO. This letter gives the results from an IR and

XPS investigation of AS–M_xO_y calcined below 773 K and suggests a scheme for the transformation between the isolated and the bidentately sulfate ion involved in the active sites in SPMO.

2. Experimental

TiO_2 (anatase) with a surface area of 180 m^2/g, prepared as described in ref. [6], was taken as a model of the metal oxides. It was immersed into a solution of ammonium sulfate, followed by evaporation to dryness, by milling thoroughly and by calcining at different temperatures for 2 h, to give the samples tested in this paper. They are designated AS–TiO_2(K), where K refers to the temperature at which the sample was obtained. The content of sulfur, based on SO_3, is 6%.

AS–TiO_2(K) was mixed with KBr at a weight ratio of 1:300, then milled and pressed into a wafer of 10 mg/cm^2 for IR measurements (Nicolet 5DX FT-IR spectrometer).

The surface atom percentages of the samples were measured by the method described in ref. [7] (VG ESCALAB MK II).

3. Results and discussion

3.1. CHANGE OF IR SPECTRA OF AS–TiO_2(K) WITH TEMPERATURE

Fig. 1 illustrates the change of IR spectra of AS–TiO_2(K) with the treatment temperature. The spectrum of AS–TiO_2(423), in fact, is made up by overlapping the spectra of TiO_2 and ammonium sulfate. The absorption band at 1400 cm^{-1} is assigned to the bending frequency of H–N–H and the one at 1119 cm^{-1} to the stretching frequency of S=O. This spectrum implies that ammonium sulfate has not yet interacted with TiO_2 in this sample. When the treatment temperature reaches 473 K, absorption bands at 1249, 1138, 1048 and 974 cm^{-1} appear instead of the absorption band at 1119 cm^{-1}. Also the intensity of these absorption bands increases with the treatment temperature until 573 K. These absorption bands were assigned to the bidentately bound sulfate ion (BBSI) [1,8]; the absorption bands at 1249, 1138 and 1048 cm^{-1} to ν_3 of BBSI; the absorption band at 974 cm^{-1}, to ν_1 of BBSI.

The appearance of the absorption bands at 1249, 1138, 1048 and 974 cm^{-1} instead of the absorption band at 1119 cm^{-1} is due to a decrease in symmetry of SO_4^{-2} from T_d in the isolated form to C_{2v} in the bidentately bound form.

Connecting the occurrence of these bands with other results from the IR and XPS investigation, Yamaguchi and Tanabe proposed that BBSI is coordinated to M in metal oxide, thus forming a surface sulfato complex of M involved in the

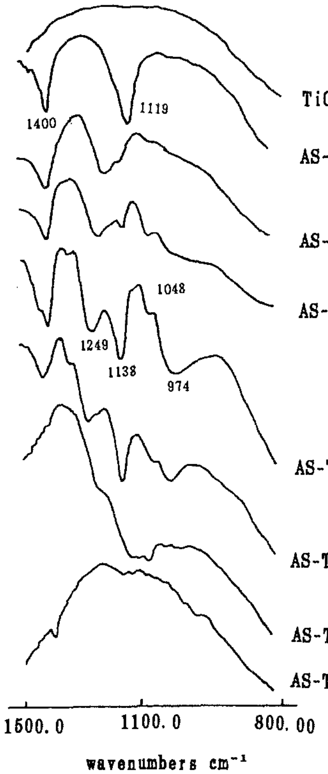
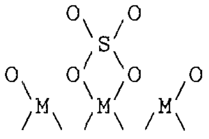


Fig. 1. Change of IR spectra of ammonium sulfate–titanium oxide with the temperature.

sites responsible for the acidity and the catalytic activity of SPMO [1]. The structure of the sulfato complex is



where the M can act as Lewis acid sites.

Therefore, from our IR results it follows that at ≈ 473 K the sulfato complex has already been formed and its amount increases with the treatment temperature until 573 K. After the appearance of the characteristic IR absorptions of BBSI the band at 1400 cm^{-1} still has some intensity until 573 K. This may mean that there is a certain amount of NH_4^+ on the surface, which might act as a balance cation of the sulfato complex.

3.2. TREATMENT OF AS–TiO_2(K) WITH AMMONIA

To observe the chemical stability of BBSI, AS–TiO_2(573) is subjected to ammonia treatment at room temperature for 2 h, thereupon producing the

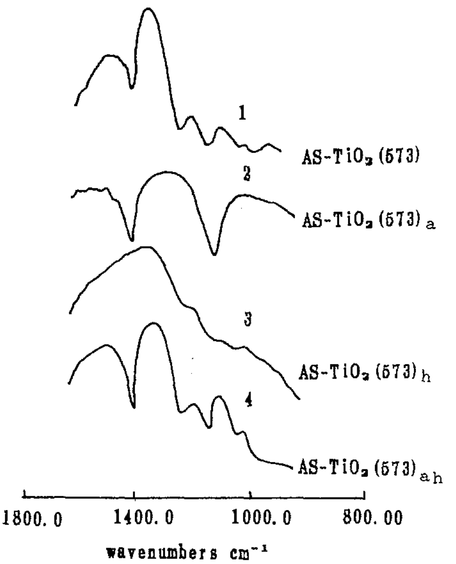


Fig. 2. Change of IR spectra of ammonium sulfate–titanium oxide with the treatment condition.

sample AS–TiO$_2$(573)$_a$. As can be seen from fig. 2, the absorption bands characteristic of BBSI disappear by the ammonia treatment while the one of the isolated sulfate ion reappears.

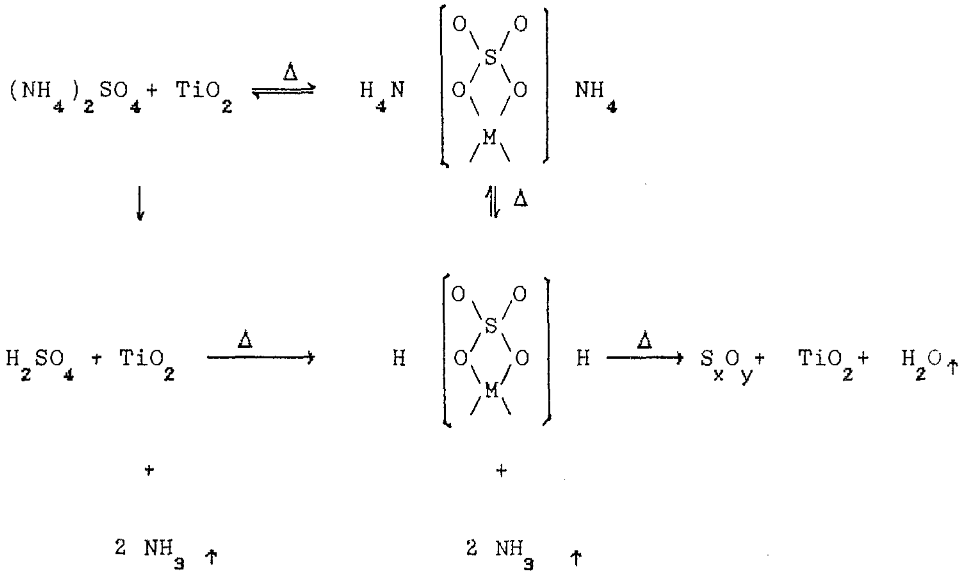
More interesting is that heating AS–TiO$_2$(573)$_a$ at 573 K for 2 h (giving AS–TiO$_2$(573)$_{ah}$) can lead to reappearance of the characteristic absorptions of BBSI (spectrum 4).

The same result is observed for AS–TiO$_2$(473) and AS–TiO$_2$(523).

The above results reveal that for the AS–TiO$_2$ system the appropriate thermal treatment can cause the isolated sulfate ion to be transformed into BBSI, while the latter can be converted into the former by action of ammonia. That is to say, the transformation between the isolated sulfate ion and BBSI is reversible on certain conditions. The reversible transformation can be postulated to proceed by scheme 1.

According to this scheme, by thermally treating AS–TiO$_2$ a species $(NH_4)_2[{=}TiSO_4]$, referred to as the NH$_4$-form of the sulfato complex, is formed first. Upon subsequent heating it decomposes by loosing NH_3, thus forming the H-form of the sulfato complex, $H_2[{=}TiSO_4]$. In more severe conditions the H-form of the complex decomposes becoming S_xO_y, H_2O and TiO_2. S_xO_y may escape into the space or penetrate into the bulk of TiO_2. The proton left as a result of the decomposition of NH_4^+ is delocated. It might be the origin of the Brønsted acidity of SPMO prepared from ammonium sulfate–titanium oxide.

It is possible that the H-form and the NH$_4$-form of the sulfato complex co-exist on some samples, depending on the treatment temperature.



Scheme 1.

Another possible way to the H-form of the sulfato complex is by the interaction of sulfuric acid produced by decomposition of ammonium sulfate with Ti.

The scheme postulated has some support from the data of XPS (table 1) and from the other experimental results.

3.3. XPS MEASUREMENT

As measured by XPS, the surface N/S ratio of $(NH_4)_2SO_4$ is 1.27, but that of AS–TiO_2(573) is only 0.63. This may be indicative of the decomposition of NH_4^+. For AS–$TiO_2(573)_a$ the surface N/S ratio rises to 0.80. This means that during the treatment with ammonia nitrogen penetrates again into the surface

Table 1
XPS data of AS–TiO_2 samples

Samples	Surface atom percentages				N/S ratio
	N	S	Ti	O	
$(NH_4)_2SO_4$	25.56	20.22	–	54.21	1.27
AS–TiO_2(573)	12.46	19.89	6.27	61.37	0.63
AS–$TiO_2(573)_a$	15.04	18.80	5.54	60.68	0.80
AS–$TiO_2(573)_h$	0.80	3.46	42.67	53.06	0.23
AS–TiO_2(673)	5.78	18.20	9.47	66.54	0.32
AS–TiO_2(773)	3.68	15.15	19.51	66.78	0.24
AS–TiO_2(873)	0.88	2.36	26.36	70.44	0.37

of the sample from the gaseous phase, as shown by the reverse process in scheme 1.

According to the scheme the decomposition of NH_4^+ is independent of that of BBSI. More severe conditions (longer treatment time or higher treatment temperature) are needed for the BBSI–Ti group to decompose.

It is certainly shown that

(1) the drop of the surface N percentage with increasing treatment temperature is faster than that of the surface S percentage (table 1);

(2) prolongation of treatment at a fixed temperature can lead to the decrease of the intensity of the absorption bands characteristic of BBSI (spectrum 3, fig. 2) and to the decrease of the surface S percentage (the datum of AS–$TiO_2(573)_h$, the sample obtained by treating AS–TiO_2(573) at 573 K for 16 h, in table 1).

(3) Increasing the treatment temperature keeping the time fixed also leads to a result similar to that in (2) (the spectra in fig. 1 and the data in table 1, of AS–TiO_2(673), AS–TiO_2(773) and AS–TiO_2(873)).

3.4. TREATMENT OF H_2SO_4–TiO_2

By treating the H_2SO_4–TiO_2 system under certain conditions one can also obtain the sample which gives the spectrum showing the characteristic absorptions of BBSI but not the 1400 cm^{-1} band. Still, when this sample is treated with ammonia, its spectrum resembles that of AS–$TiO_2(573)_a$. This result signifies that heating H_2SO_4–TiO_2 might directly produce the H-form of the sulfato complex. Thus, once it reacts with ammonia, ammonium sulfate can be produced too.

2.5. ACIDITY AND CATALYTIC ACTIVITY OF AS–TiO_2(K)

The catalytic activity of the samples for the esterification of butanol with propionic acid (at 403 K for 5 h) can be ordered in the following sequence:

$$\begin{aligned} \text{AS–TiO}_2(573) &\approx \text{AS–TiO}_2(573)_{ah} > \text{H}_2\text{SO}_4 \approx \text{AS–TiO}_2(673) \\ &> \text{AS–TiO}_2(773) \approx \text{AS–TiO}_2(573)_h > \text{AS–TiO}_2(873) \\ &\gg \text{AS–TiO}_2(423) \approx \text{AS–TiO}_2(573)_a. \end{aligned}$$

IR results show that on AS–TiO_2(423) and AS–$TiO_2(573)_a$, which have the lowest activity, there is no sulfato complex (figs. 1 and 2). After pyridine absorption (carried out in vacuum cell), in IR spectra of these two samples the bands at 1540 and 1450 cm^{-1} are not observed, meaning the absence of Brønsted and Lewis acidity. Instead, on AS–TiO_2(573) and AS–$TiO_2(573)_{ah}$ not only the characteristic absorptions of BBSI but also the bands showing Brønsted and Lewis acidity are observed. Also, both the Brønsted and Lewis acidities of these two samples are stronger than those of any other samples. As expected from the scheme, the Brønsted acidity of the samples originates from the acidic hydroxyl group formed by thermally removing NH_3. The hydroxyl group can in principle be probed by monitoring the OH bands by IR. However, for the present time only a blurred broad absorption in the OH region is observed. Perhaps there are two factors interfering with the observation of the distinct acidic hydroxyl. One is that there might be some kinds of oxygen species in different chemical surroundings being able to form the hydroxyl because of the delocalization of the proton left by the decomposition of NH_4^+, after the formation of the sulfato complex. The other is the interference from the chemically adsorbed water. Such water is likely to be on the sample, since the samples cannot be treated in vacuum cell at temperatures higher than its preparation temperature.

Obviously, the inactivity of AS–TiO_2(423) and AS–$TiO_2(573)_a$ is related to the absence of the sulfato complex, whereas the high activity of AS–TiO_2(573) and AS–$TiO_2(573)_{ah}$ may imply a high concentration of the H-form of the sulfato complex, since they have the strongest Brønsted acidity.

3.6. TREATMENT OF THE SAMPLE WITH ALCOHOLIC SOLUTION OF NaCl

Scheme 1 shows that NH_4^+ in $(NH_4)_2[{=}TiSO_4]$ should be exchangeable. To examine this, the concerned sample is treated with an alcoholic solution of NaCl. An aqueous solution cannot be used since the sulfato complex is water soluble.

After treatment with the saturated alcoholic solution of NaCl, AS–TiO_2(573), or AS–TiO_2(523) and AS–TiO_2(673), gives a spectrum showing the characteristic absorption of BBSI but not the band at 1400 cm^{-1}. This fact may be support for the presence of $(NH_4)_2[{=}TiSO_4]$ in this sample.

Additional experimental investigation is being carried out to verify further the validity of the postulated scheme.

4. Conclusion

Treating ammonium sulfate–titanium oxide below 573 K can cause the isolated sulfate ion to be transformed into the bidentately bound sulfate ion essential for the acidic and the catalytically active sites of sulfate promoted metal oxide, while by action of ammonia the bidentately bound sulfate ion can be converted to the isolated sulfate ion. There might be two forms of surface sulfato complex containing the bidentate sulfate ion, H-form and NH_4-form, on the samples of sulfate promoted metal oxides obtained below 573 K. Above 573 K the bidentately bound sulfate ion will decompose gradually with further increase of the treatment temperature.

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