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Characterization and reactivity of pure TiO_2–SO_4^{2-} SCR catalyst: influence of SO_4^{2-} content

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Abstract

The modifications of textural and surface properties of sulfated TiO_2 have been investigated by means of XRD, surface area, XPS, Raman, FT-IR, NH_3-TPD, and catalytic tests in the reduction of NO by NH_3. According to sulfate content, the isolated sulfate transforms to a polynuclear sulfate type. Between SO_4^{2-}=3.0 and 6.6 wt.%, the amount of S=O species per unit area is almost constant and equal. Total number of acid sites increases with the SO_4^{2-} content, while the strongest sites are maximum at 1.5 wt.% loading. The areal TOF (turnover frequency, mole NO converted/s m^2) is also higher at SO_4^{2-}=1.5 wt.% and is directly related to the number of strong Lewis acid sites. Accordingly, it is suggested that the strong Lewis site generated by doping TiO_2 with SO_4^{2-} is responsible for the higher reactivity of TiO_2–SO_4^{2-} at high temperature. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Titania sulfate; SCR

1. Introduction

The elimination of nitrogen oxides emitted from the combustion process is particularly important in the reduction of the environmental problems caused by the formation of acid rain and depletion of ozone through the secondary reactions in atmosphere.

Various processes have been proposed for the elimination of NO_x through widespread application of available methods and/or via the development of new technologies [1]. Amongst them, the SCR (selective catalytic reduction) is considered as the most efficient technology. The usual catalyst of SCR process consists of V_2O_5 and TiO_2 as main components. Since this type of catalyst is used in industrial plants and satisfies the user as far as efficiency is concerned, the behavior of the different active components such as V, W, Mo as well as their interaction with the support have been deeply investigated.

However, in the specific condition of SCR there is still some problem since severe conditions of SCR reaction induce side reactions and catalyst deactivation. For example, when the temperature of SCR reaction exceeds 400°C, a decrease of the activity and selectivity of the catalyst mainly due to production of NO and NO_2 caused by ammonia oxidation is observed [2–3].

Accordingly, some researchers have proposed various attempts to overcome such problems on SCR catalysts [4–5]. Amongst them, the choice of an SO_4^{2-} ion as TiO_2 promoter is attractive since it has a high activity in high temperature reactions between 400 and 600°C [6]. It has been proposed that the sulfate produces a strong acidic site at high temperature [7–11], and this can lead to the high reactivity of the SCR reaction without by-products.

However, until now, no in-depth interpretation of the interaction between TiO_2 and SO_4^{2-} has been

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proposed. Furthermore, in the SCR process, the role of SO_4^{2-} in pure TiO_2–SO_4^{2-} catalysts could not be explained on the basis of conventional SCR mechanisms [12].

Accordingly, this work is mainly focused on the change of physicochemical properties caused by the TiO_2–SO_4^{2-} catalyst with variable SO_4^{2-} content and then correlated with deNO$_x$ properties.

2. Experiment

2.1. Preparation of catalysts

$Ti(OH)_4$ was prepared by precipitation of a solution of titanium tetrachloride. 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. To consider the decomposition of sulfate due to the thermal stability, the real loading amounts of sulfate after calcination were verified by the elemental analysis.

2.2. Characterization

The elemental analyses (Ti, S) were performed by inductively coupled plasma-optical emission spectroscopy (ICP-OES).

The specific surface areas of the samples were measured by the BET method with a Micromeritics ASAP 2000 equipment using nitrogen at −196°C. Prior to measurements, all samples were outgassed at 150°C until vacuum was reached at 1×10^{-5} Torr.

The X-ray diffraction patterns were recorded using a Siemens D-5000 powder diffractometer with nickel filtered Cu Kα radiation (λ=1.5404 Å). The step scans were taken over the range of 2θ from 5 to 80.

The 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. 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.

The Raman spectra were measured with a Dilor Instrument S.A. spectrometer with the 632 nm line of Ar ion laser as excitation source under ambient conditions. The number of scans is 5 and the time of accumulation is 5 s per scan.

An NH_3-TPD (temperature programmed desorption) spectrum was obtained by monitoring the desorbed ammonia, after adsorbing ammonia 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 flow rate (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 disks, 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 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 at 400°C.

2.3. Catalytic activity measurement

Activity measurements were performed in a continuous flow fixed bed reactor operating at atmospheric pressure. GHSV (h^{-1}) was 46 000. The total flow rate was 100 ml/min and feed composition was: nitric oxide 0.1 vol.%; ammonia 0.105 vol.%; 2.5 vol.% oxygen, in helium. The inlet and outlet gas compositions were measured using a quadrupole mass spectrometer QMC 311 Balzers coupled to the reactor. All conversions were measured at the steady state achieved, under our experimental conditions, after 30–40 min at 400°C.

3. Results and discussion

3.1. Structure and morphology

The use of titanium hydroxide as sulfated precursor should *induce textural* modifications of samples

Table 1
Structure and textural data

$SO_4{}^{2-}$ loading (wt.%)	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

during the calcination, since the concentration of hydroxides on the particles which are able to lead to the agglomeration in the particle and/or between particles is modified by the sulfation.

Table 1 shows structure and textural data along with the increase of the $SO_4{}^{2-}$ ion contents. BET surface area is proportional to the amount of loaded sulfate and an increase of 7 m^2/g wt.% $SO_4{}^{2-}$ is observed. The average pore diameter of all TiO_2 sulfate samples is constant. It is known that the degree of agglomeration at constant pore diameter can be controlled by the concentration of the free hydroxide in the particle without the decrease of the number of bonds between particles [13]. Accordingly, this type of agglomeration occurring in TiO_2–$SO_4{}^{2-}$ indicates that the free OH bond sites of $Ti(OH)_4$ in the particle, where the agglomeration/crystallization takes place during calcination, are contacted by the addition of $SO_4{}^{2-}$ ion.

Fig. 1 shows the relation of calculated sulfate density per unit area with the S/Ti ratio measured by XPS. The S/Ti ratio is linearly proportional to the sulfate concentration. This linearity evidences the homogeneous distribution of sulfate in all the samples.

3.2. *Type of* $SO_4{}^{2-}$ *species adsorbed on* TiO_2

From the BET surface area and the sulfate contents, the number of S (atoms/m^2) can be calculated and considering a surface concentration 7 atoms/nm^2 of Ti, the atomic S/Ti ratio of S/Ti can also be evaluated. This is shown in Table 2. The atomic ratio S/Ti increases with sulfate content and a maximum value of 0.59 when $SO_4{}^{2-}$=6.6 wt.% is obtained. Saur et al. [14] using isotope exchange and IR analysis proposed a $(Ti–O)_3S$=O structure under dry conditions. Therefore, based on this structure, the 0.33 S/Ti atomic ratio is considered as a maximum value under dry conditions.

The S/Ti ratio up to 3.0 wt.% $SO_4{}^{2-}$ catalyst is not over the maximum value of 0.33, but at higher concentration of $SO_4{}^{2-}$ (6.6 wt.%), although the surface area is increased according to the increase of sulfate amounts, the S/Ti ratio is 0.59. This evidences that the S=O structure is not $(Ti–O)_3S$=O at high $SO_4{}^{2-}$ concentration. In other words, the sulfate type changes from tridentate species to bidentate species with $SO_4{}^{2-}$ content. As the sulfate loading is increased, it is proposed that $S_2O_7{}^{2-}$ and $S_3O_{10}{}^{2-}$ species may also be present [15–18].

To identify the S=O species in sulfate complex, FT-IR is a very useful method and has been widely used. IR spectra of sulfated metal oxides normally present a strong absorption band near 1380–1360 cm^{-1} and a broad band around 1000–1200 cm^{-1}.

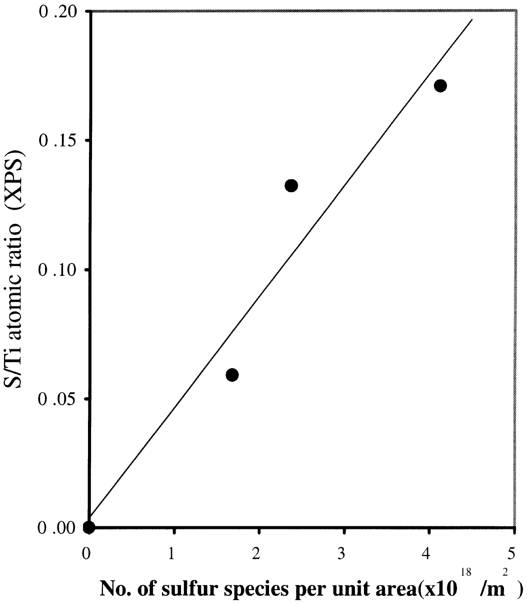

Fig. 1. Dispersion of sulfate on the surface of TiO_2.

Table 2
Distribution of sulfate and calculated data

SO_4^{2-} loading (wt.%)	Total number of SO_4^{2-} (1×10^{18}/g)	Number of %SO_4^{2-} ($1\times10^{18}/m^2$)	Total number of surface Ti atom (1×10^{18}/g) [7 Ti/nm^2]	S/Ti atomic ratio
0	0	0	280	0
1.5	97.3	1.7	336	0.23
3.0	198.6	2.4	588	0.33
6.6	428.3	4.1	728	0.59

In all the samples, after pretreatment at 400°C, a very intensive peak is observed at around 1370 cm^{-1}, and can be attributed to S=O stretching vibration mode.

Fig. 2 presents the relation of the concentration of S=O per unit area with the concentration of sulfate. Up to SO_4^{2-}=3.0 wt.%, the amount of S=O increases and then reaches a plateau. This shows that the S=O concentration decreases at high sulfate content. This would confirm that the generation of bidentate sulfate at 6.6 wt.% is due to polynuclear sulfate at the expense of isolated sulfate.

The different proportion of S=O between the isolated and polynuclear sulfate may be distinguished and confirmed by Raman spectroscopy. As previously reported, Raman spectroscopy is an excellent tool to detect the double bond according to the change of environment. It is well known that the range between 900 and 1100 cm^{-1} is sensitive to the change of double bond stretching and used to analyze some SCR catalysts such as V_2O_5, WO_3 and V_2O_5/WO_3 [19].

The Raman spectra for TiO_2 sulfate samples, recorded under ambient conditions, are presented in Fig. 3. In pure TiO_2, no peak is detected in this region. When the amount of sulfate increases up to 1.5 wt.%, a peak located at 1001 cm^{-1} is observed. Assignment based on the FT-IR results and evaluation of S/Ti ratio, indicates that the peak at 1001 cm^{-1} is due to the S=O bonds of the isolated sulfate. As the amount of sulfate on the catalyst increases, the intensity of 1001 cm^{-1} is not only increased, but a new peak at 1040 cm^{-1} is also generated. It is evident that this newly created peak at increasing sulfate density is induced by the S=O bonds of the polynuclear sulfate type. Thus, the surface sulfate at 3.0 and 6.6 wt.%

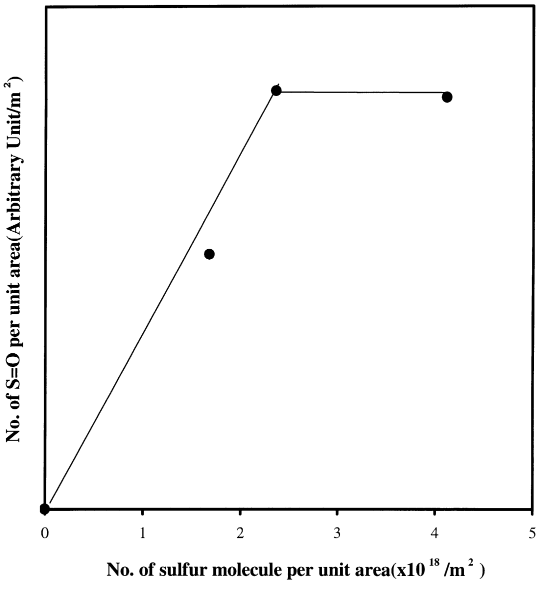

Fig. 2. Peak position and relative concentration of S=O obtained from FT-IR according to the sulfur density per unit area.

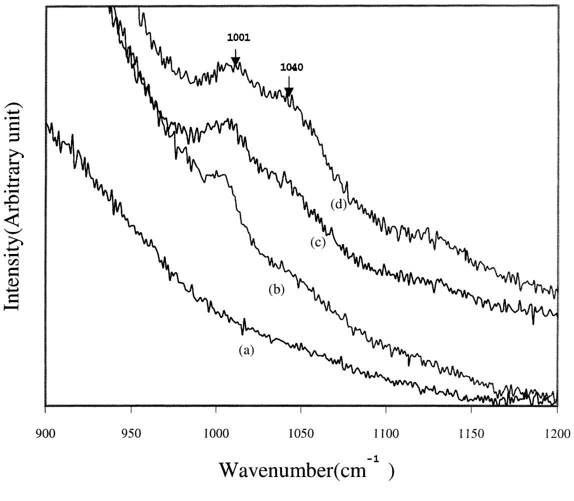

Fig. 3. Raman spectra: (a) TiO_2; (b) TiO_2–SO_4^{2-} (1.5 wt.%); (c) TiO_2–SO_4^{2-} (3.0 wt.%); (d) TiO_2–SO_4^{2-} (6.6 wt.%).

appears to be constituted of isolated sulfate species and polynuclear sulfated species.

3.3. Acidity generation by adsorbed sulfate

The S=O structure is essential for the generation of acidic sites on sulfate promoted oxide samples. The strong ability of S=O in sulfate complexes to accommodate electrons from a basic molecule is a driving force in the generation of highly acidic properties [20,21].

The acidic properties generated by the inductive effect of S=O bonds of the complex are strongly affected by the environment of the sulfate ion. Thus, it can be proposed that acid properties would be modified by both the type of S=O in the sulfate complex and the coverage of sulfate on the surface. As mentioned above, the increased loading of sulfate on TiO_2 can form the polynuclear type of sulfate complex and increase the coverage of the Ti metal ion by the sulfate ion.

Accordingly, in order to investigate the effect of the type of S=O bonds on the acidity, NH_3-TPD experiments were carried out. The results are shown in Fig. 4. The amount of NH_3 desorbed up to 500°C increases according to the increase of sulfate ion. The feature of NH_3 desorption of TiO_2–$SO_4{}^{2-}$ is quite different from that of pure TiO_2. In the case of pure TiO_2, the major desorption of NH_3 occurred from 100 to 320°C and a small peak due to strongly adsorbed ammonia on surface is detected at 400°C. In the 1.5 wt.% sulfated catalyst, the amount of NH_3 desorbed between 200 and 300°C is reduced and the main desorption of NH_3 appears between 300 and 400°C. Therefore, it seems that the medium acid sites in TiO_2 transform to strong acid sites by addition of sulfate. For the 3.0 and 6.6 wt.% sulfate, the feature of TPD spectra is similar to that of the 1.5 wt.% sulfated catalyst. But as compared with the 1.5 wt.% sulfated catalyst, the peak attributed to the strong acid site gradually shifts to 345 and 321°C, whereas the peak due to weak acid site appears at the same temperature around 200°C.

To quantitatively analyze the relation between the generation of acid sites and the sulfate loading, the amount of NH_3 desorbed during NH_3-TPD was measured. Fig. 5 shows the relation between the number of adsorbed ammonia per unit surface area with sulfate contents per unit area. The initial increase of NH_3, after sulfate loading up to 1.5 wt.%, correspond to the increased rate of 0.18 NH_3 molecules per sulfate molecule. An additional increase of sulfate leads to a decrease of the number of NH_3 molecules

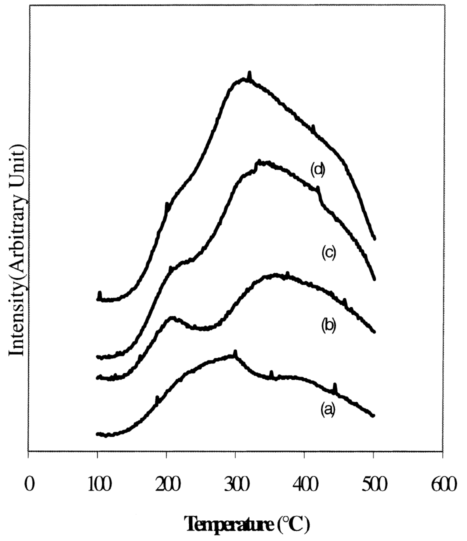

Fig. 4. NH_3-TPD spectra: (a) TiO_2; (b) TiO_2–$SO_4{}^{2-}$ (1.5 wt.%); (c) TiO_2–$SO_4{}^{2-}$ (3.0 wt.%); (d) TiO_2–$SO_4{}^{2-}$ (6.6 wt.%).

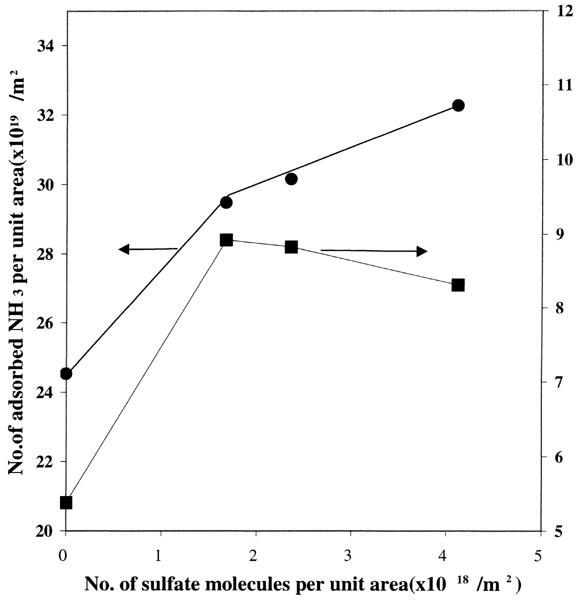

Fig. 5. The generation of acidity and acid strength in NH_3-TPD: (●) from 100 to 500°C; (■) from 400 to 500°C.

per sulfate molecule to 0.15 at 3.0 wt.% and 0.12 at 6.6 wt.%, although the total amount of NH_3 adsorbed increases due to an increase of both sulfate contents and surface area. Besides, the proportion of strong acidic sites to total acid sites decreases to 60 and 33% with the increase of the number of sulfate molecules per surface area. This reduction of strong acid sites is also consistent with the shift of temperature mentioned above in the TPD experiments. Considering the results of the sulfate species and S/Ti ratio according to sulfate contents, it appears that the generation of total and strong acidity is not affected by the type of sulfate species, such as isolated and polynuclear, but by the coverage of the surface of the Ti by sulfate ions. Accordingly, it is concluded that the free Ti ion surrounding the sulfate is responsible for the generation of strong acid sites.

With respect to the kind of acid site, it has been reported that both Lewis and Brønsted acid sites can be generated when a sulfate ion is introduced into TiO_2 [6,11]. In order to investigate the effect of the type of sulfate on the generation of Brønsted and Lewis acid sites and to specify their strength, the concentration of both acid sites is compared using the peak areas measured by FT-IR after NH_3 adsorption. The Brønsted and Lewis acid sites are assigned at 1430 and 1605 cm^{-1}, respectively. These results are shown in Fig. 6.

After evacuation at 400°C, the 1.5 wt.% sulfate catalyst contains more Lewis and Brønsted sites than both the 3.0 and 6.6 wt.% sulfate catalysts. This result is consistent with that of TPR analyzed between 400 and 500°C. Especially, the fact that the strong Lewis sites are strongly related to the neighbor Ti ion for sulfate concentration higher than 1.5 wt.% evidences the importance of sulfate coverage in the generation of strong acid sites.

3.4. DeNO$_x$ activity

In SCR reaction of NO with NH_3, there is no doubt that the acid function of catalyst is the main factor which controls the high activity, but the fundamental questions about the nature of active ammonia species or active sites are still not fully answered.

In particular, surface acidity plays an important role in the adsorption and activation of ammonia at high temperature. Chen and Yang [6] have proposed that the SCR activity of the TiO_2 sulfate catalyst is directly related to the amount of Brønsted acid sites, as confirmed by XPS. They detected a peak at 401.7 eV assigned to ammonia chemisorbed on Brønsted acid sites. However, since the adsorption of NH_3 was carried out and probably measured at room temperature in that paper, the peak of 401.7 eV cannot perfectly prove the role of Brønsted sites as an active site for SCR reaction at high temperature. The results only indicate the difference of total acidity between TiO_2 and TiO_2 sulfate.

Accordingly, the influence of sulfate content and acidity on catalytic performance for SCR reaction at high temperature was studied. From these results, a type of acid site which is directly responsible for SCR reaction at high temperature is described.

The SCR activities were measured under steady state conditions at 400°C and the NO conversion obtained over titania sulfate catalysts as a function of sulfate loading are shown in Fig. 7. No considerable N_2O and NO_2 were detected for the series of catalysts at 400°C. The NO conversion over pure TiO_2 is lower than 20%. After sulfation, all the samples show an increase of conversion up to 70–90%. The increase of activity is consistent with the amount of NH_3 adsorption shown in Fig. 6.

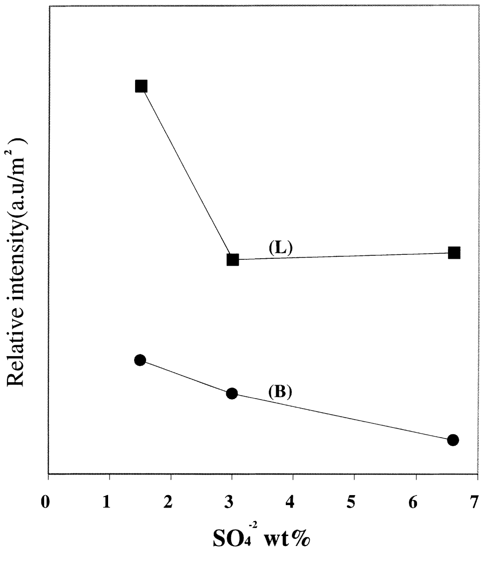

Fig. 6. Concentration of Brønsted (B) and Lewis (L) acid sites for sulfated TiO_2 samples evacuated at 400°C for 30 min, after adsorption by ammonia at room temperature.

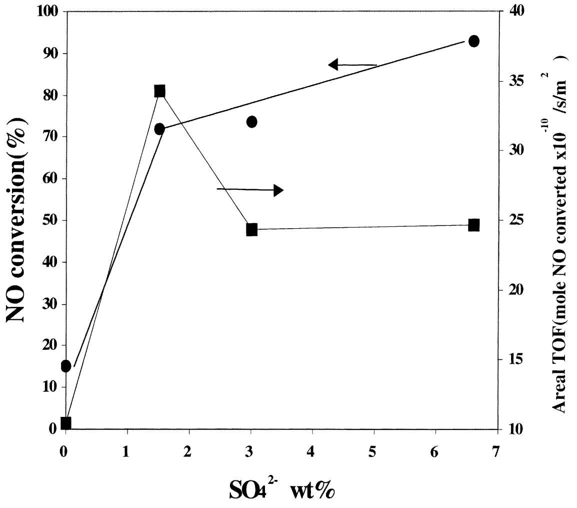

Fig. 7. NO conversion and TOF value for the SCR reaction vs. sulfate contents.

When the sulfate contents further increase in TiO_2 sulfated catalyst, the NO conversion almost linearly increases, although the increase in the rate of conversion is smaller. But, it is not easy to detect the influence of acidity and acid site, since, considering the difference of surface area, it is supposed that the difference in NO conversions is mainly affected by the increase of this parameter. Thus, for interpreting the real effect of acid sites and acidity and excluding the influence of surface area, the areal TOF value was used. Areal TOF represents the number of converted NO moles per unit time (s) and area (m^2).

The areal TOF values are compared with sulfate contents and are also shown in Fig. 7. The areal TOF of SO_4^{2-}=1.5 wt.% catalyst is superior to SO_4^{2-}=3.0 wt.% and SO_4^{2-}=6.6 wt.%. The SO_4^{2-}=3.0 wt.% is almost equal to SO_4^{2-}=6.6 wt.%. Considering the SCR mechanism, areal TOF value is correlated by the acid function, which controls the adsorption of ammonia on the catalyst surface, and the redox properties, which activate the adsorbed ammonia. In all samples based on TiO_2, since the redox properties seem to be similar, it is reasonable to suppose that the difference of areal TOF is essentially connected to the number of acid sites.

Accordingly, the higher areal TOF value in the SO_4^{2-}=1.5 wt.% catalyst shows that this catalyst has more effective active sites per unit area for SCR reaction than other catalysts. As can be seen in Fig. 6, the trend of Lewis acid sites along with the sulfate contents is consistent with that of areal TOF, whereas there is no direct relationship with the Brønsted acid sites. This relationship would indicate that the actual active site for SCR reaction on the TiO_2 sulfate catalyst is not a Brønsted acid site but a Lewis acid site.

4. Conclusions

The addition of sulfuric acid during the preparation of TiO_2, leads to an increase in the surface area and the formation of sulfate complexes at the surface.

S=O concentration on the surface decreases when the surface is saturated by sulfate ions. This is due to the formation of polynuclear sulfate species.

It is not clear that the polynuclear sulfate cannot extract as many electrons as isolated sulfate to generate a strong acidity. But the coverage of titania which can be evaluated by the S/Ti ratio is closely related to acidity and acid strength. Accordingly, the increase of sulfate amount per unit area induces a decrease of the real density of strong acidity per surface area.

The areal TOF of NO for SCR reaction is higher in the case of SO_4^{2-}=1.5 wt.%. This is due to its strong acidity at high temperature. Especially, the strong Lewis sites are directly related with $DeNO_x$ activity.

Acknowledgements

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References

[1] P. Forzatti, L. Lietti, Heterogen. Chem. Rev. 3 (1996) 33.
[2] L.J. Alemany, L. Lietti, N. Ferlazzo, P. Forzatti, G. Busca, E. Giamello, F. Bregani, J. Catal. 155 (1996) 117.
[3] J.P. Chen, R.T. Yang, J. Catal. 80 (1992) 135.
[4] P. Wauthoz, M. Ruwet, T. Machej, P. Grange, Appl. Catal. 69 (1991) 149.
[5] J. Blanco, A. Bahamonde, E. Alvarez, P. Avila, Symposium on Reduction of NO_x and SO_x from Combustion Sources, in: Proceedings of the 214th National Meeting, Am. Chem. Soc., 1997, p. 818.
[6] J.P. Chen, R.T. Yang, J. Catal. 139 (1993) 277.

[7] K. Tanabe, M. Itoh, K. Morishige, H. Hattori, in: Proceedings of the International Symposium on Preparation of Catalysts, Brussels, 1975, p. 65.

[8] H. Hino, K. Arata, J. Chem. Soc., Chem. Commun. (1979) 1148.

[9] Y. Tsutomu, Appl. Catal. 61 (1990) 1.

[10] M. Waqif, J. Bachelier, O. Saur, J.C. Lavalley, J. Mol. Catal. 72 (1992) 127.

[11] J.R. Sohn, H.J. Jang, J. Catal. 136 (1992) 267.

[12] G. Busca, L. Lietti, G. Ramis, F. Berti, Appl. Catal. B 18 (1998) 1.

[13] J.F. Le Page, J. Cosyns, P. Courty, E. Freund, J.P. Franck, Y. Jacquin, B. Juguin, C. Marcilly, G. Martino, J. Miquel, R. Montarnal, A. Sugier, H. Van Landeghem, Applied Heterogeneous Catalysis, Editions Technip, Paris, 1987, p. 92 (Chapter 5).

[14] O. Saur, M. Bensitel, A.B. Mohammed Saad, J.C. Lavalley, J. Catal. 99 (1986) 104.

[15] M. Bensitel, O. Saur, J.C. Lavalley, B.A. Morrow, Mater. Chem. Phys. 19 (1988) 147.

[16] C. Morterra, G. Cerrato, C. Emanuel, V. Bolis, J. Catal. 142 (1993) 349.

[17] C. Morterra, G. Cerrato, V. Bolis, Catal. Today 17 (1993) 505.

[18] M. Trung Tran, N.S. Gnep, G. Szabo, M. Guisnet, Appl. Catal. 171 (1998) 207.

[19] M.A. Vuurman, I.E. Wachs, A.M. Hirt, J. Phys. Chem. 95 (24) (1991) 9928.

[20] R.J. Gillespie, E.A. Robinson, Can. J. Chem. 41 (1963) 2074.

[21] T. Yamaguchi, T. Jin, K. Tanabe, J. Phys. Chem. 90 (1986) 3148.