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Adsorption and interaction of H_2S/SO_2 on TiO_2

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Abstract

Adsorption and interaction of H_2S/SO_2 on titania as well as on alumina for comparison has been studied by temperature programmed desorption (TPD), infrared (IR) spectroscopy and temperature programmed electronic conductivity (TPEC) techniques. It was found that the adsorption of both H_2S and SO_2 on TiO_2 is much greater than on Al_2O_3. The electronic conductivity of TiO_2 measured by TPEC varies significantly as adsorption and desorption takes place on TiO_2, showing a strong interaction between TiO_2 and adsorbates. At temperature above 200°C, H_2S or SO_2 adsorbed on TiO_2 can be converted into S, H_2O and SO_2 or SO_3. While on the hydrogen treated TiO_2, H_2S is decomposed into S and H_2, SO_2 into S. The active sites on TiO_2 surface cannot be so strongly adsorbed by SO_2 that it is much more resistant to the sulfation reaction. Unlike TiO_2, Al_2O_3 only provides surface adsorption sites, which can be readily sulfated. The data obtained support one's understanding why TiO_2 exhibits a better catalytic performance than that of Al_2O_3 as a Claus reaction catalyst. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Titania; The Claus reaction; Hydrogen sulfide

1. Introduction

The Claus reaction is a well known process for the recovery of sulfur from acidic gases containing hydrogen sulfide. In the modified Claus reaction, hydrogen sulfide is first oxidized to SO_2 and then the catalytic reaction between SO_2 and the rest of H_2S takes place to produce sulfur and water:

$$2H_2S + SO_2 = 2H_2O + 3/xS_x$$

In practice, γ-Al_2O_3 has long been used as the catalyst for the Claus reaction. However, it was often found that γ-Al_2O_3 is readily deactivated due to the formation of sulfate or strongly adsorbed species on the catalyst surface [1,2]. Moreover, the presence of a small amount of oxygen in the reactant gases may lead to a dramatic decrease of the catalytic activity. Since 1980, it has been increasingly reported that TiO_2 based catalysts show superior catalytic properties to Al_2O_3 for the Claus reaction [3].

In the past, the adsorption of SO_2, H_2S on Al_2O_3 as well as the catalytic properties of Al_2O_3 had been the subject of numerous studies [4–8]. Nevertheless, the studies on the adsorption of SO_2 and H_2S on TiO_2 have been limited to a few reports. Saussey et al. [9] and Beck and White [10] investigated the adsorption of H_2S on TiO_2 of both anatase and rutile structures by TPD, Auger Electron Spectroscopy (AES) and IR. They found that the dissociative adsorption occurs on

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rutile but not significantly on anatase. They identified two adsorption states of H_2S on anatase but an additional third state on rutile. In the present study, the adsorption of H_2S and SO_2 on TiO_2 as well as hydrogen treated TiO_2 has been studied by TPD, IR, and TPEC. The effect and role of oxygen, low valence titanium ion and oxygen vacancy on the adsorption and interaction of H_2S and SO_2 on TiO_2 have been examined. Comparison of the adsorptive and the catalytic properties between TiO_2 and conventional Al_2O_3 catalysts has been made.

2. Experimental

2.1. *Catalyst preparation*

The catalysts were prepared by hydrolysis of titanium sulfate in $NH_3{\cdot}H_2O$, rinsed with de-ionized water until free of SO_4^{2-}, dried at 110°C, and finally, calcined at 500°C for 3 h. The specific surface area was 64 m^2/g measured by BET method. The catalysts were found to be an anatase structure by XRD.

2.2. *TPD, TPEC*

TPD and TPEC were performed in an atmospheric reactor system. N_2, as the carrier gas, was purified by passing through a 5 Å molecular sieve trap and an oxygen trap (401 oxygen removal catalyst, China) prior to experiments. The samples were pre-treated under pure N_2 gas flow while heated to 500°C at a rate of 18°C/min to scavenge impurities on the surface. Then the samples were exposed to H_2S or SO_2 for adsorption at room temperature, followed by TPD and TPEC measurements under a pure N_2 flow (25 ml/min) at a heating rate of 11°C/min. The desorbed gases were analyzed by an on-line gas chromatography (GC) equipped with a Porapak Q and a 5 Å molecular sieve columns. TPD and TPEC as well as IR experiments were also carried out on hydrogen treated TiO_2[H] samples. Hydrogen treatment of TiO_2 was conducted at 500°C under a H_2 flow for 0.5 h.

2.3. *IR measurements*

The samples were first evacuated at 400°C for 2 h to clean the surface, then cooled to room temperature. The adsorbate was introduced at 8665.9 Pa for H_2S or 1333.2 Pa for SO_2. Following the treatments at various temperatures, the IR spectra were obtained at room temperature with a Perkin-Elmer 983 instrument.

TiO_2 powder was placed between two glass surfaces and pressed into a wafer by hydraulic force. The sample was then placed in a quartz sample holder and loaded in a vacuum quartz IR cell. The sample could be moved between a furnace area and the optical path with a magnet. Calcium fluoride windows were used for the optical path.

2.4. *Evaluation of catalytic activity*

One ml catalyst was used for catalytic activity evaluation in a quartz fixed-bed reactor at 230°C and at a space velocity of 1000 or 5000 h^{-1}. The compositions of reactants were typically 3 vol% H_2S, 1.5 vol% SO_2 (N_2 balance) for the Claus reaction, 1 vol% CS_2, 20 vol% H_2O (N_2 balance) for CS_2 hydrolysis reaction. Severe sulfation experiments were carried out at 450°C and a ratio of air to SO_2 of 7:3.

3. Results and discussion

3.1. *Adsorption and interaction of H_2S on TiO_2*

3.1.1. *TPD and IR*

Fig. 1 shows the TPD profiles of H_2S adsorption on different samples. Two desorption peaks were observed on TiO_2 during the experiment, with peak temperatures at around 150°C and 350°C. The lower temperature peak was identified to be H_2S, the higher temperature peak to be SO_2 by the on-line GC. Gas

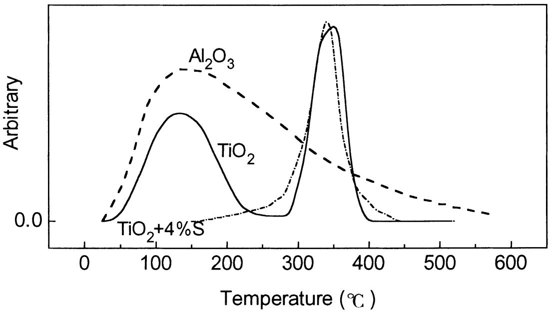


Fig. 1. H_2S TPD desorption spectra on different samples.

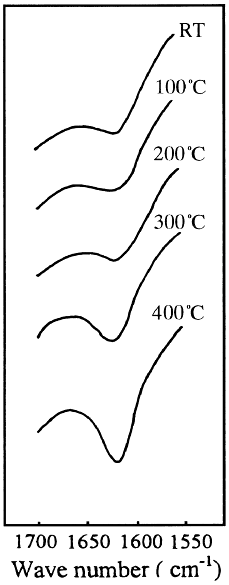


Fig. 2. IR spectra of H_2S on TiO_2 after H_2S adsorption and then treated at various temperatures.

samples were taken at the increasing edges of lower and higher temperature peaks. Sulfur deposition on the reactor wall was also noticed during the experiments. An additional TPD experiment on a sample of TiO_2+4 wt% S mixture gave a TPD pattern as shown in the same figure, indicating that sulfur in TiO_2+4 wt% S mixture could be oxidized into SO_2 in the presence of TiO_2 catalyst. TiO_2+4 wt% S mixture was made from sulfur and TiO_2 powders, which was mechanically mixed, then pelleted and smashed into 20∼30 mesh particles.

Compared to the TPD feature of TiO_2, the TPD spectrum of Al_2O_3 shows a broad desorption peak centered at 120°C, which was found to be H_2S. Obviously, the adsorption of H_2S on TiO_2 gives a more complicated TPD spectrum. Fig. 2 shows IR spectra of TiO_2 sample exposed to H_2S and then treated at various temperatures. The band at 1620 cm^{-1} as assigned to the adsorbed water by Datta and Ronald [11], increases obviously as the treatment temperature increases. The water band in IR spectra clearly indicates that the formation of water species is the result of the reaction between H_2S and TiO_2. Oxygen in TiO_2 takes part in H_2S conversion. As evidenced in the above TPD experiments, the H_2S adsorption on TiO_2 and Al_2O_3 are quite different. TiO_2 is much more active for H_2S adsorption and the adsorbed H_2S can desorb from the surface or react with surface oxygen. The adsorbed H_2S on Al_2O_3 is neither easily desorbed nor converted.

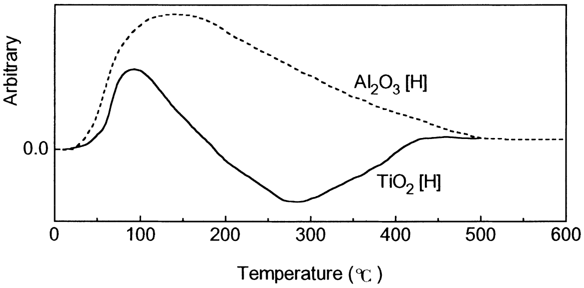


Fig. 3. TPD desorption spectra of H_2S on the hydrogen pre-treated Al_2O_3 and TiO_2 samples.

When TiO_2 was hydrogen pre-treated, TPD spectrum of H_2S as shown in Fig. 3 is quite different. It is noticed from a negative peak that H_2 desorbs at around 200°C and the peak centers at around 280°C, following the H_2S desorption peak. However, the water band in IR spectra for TiO_2[H] was not observed. For comparison, TPD spectrum of the hydrogen treated Al_2O_3 under the same conditions is shown together, which is very similar to the untreated Al_2O_3 (Fig. 1). It is well known that TiO_2 is an *n*-type semiconductor, which can be partially reduced by H_2 at high temperatures. The partial reduction can lead to the formation of oxygen vacancies and the formation of low valence titanium ions (Ti^{3+}) on the surface [12,13]. It is likely that H_2S chemisorbs at oxygen vacancy sites and sulfur occupies the oxygen vacancy sites, forming Ti–SH group. The Ti-SH groups lose hydrogen to form H_2. Beck [10] also reported that H_2 desorption occurred from a TiO_2 after adsorption by H_2S.

3.1.2. TPEC

Fig. 4 depicts TPEC results on TiO_2 and Al_2O_3, and shows, upon the adsorption of H_2S at room temperature, the conductivity of the TiO_2 sample increases rapidly by about 2–3 orders of magnitude. With increasing temperature, the conductivity first increases, passes a maximum at around 200°C, then decreases until rising again at 300°C. By contrast, the conductivity of Al_2O_3 remains almost unaffected upon the adsorption of H_2S and subsequent heating. Since TiO_2 is a semiconductor, adsorption of H_2S, an elec-

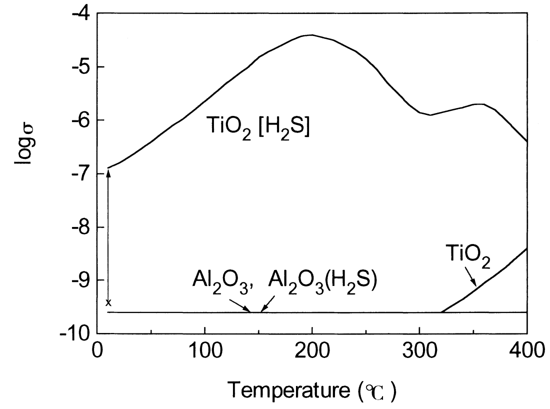
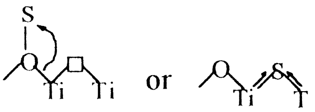


Fig. 4. TPEC profiles of Al_2O_3 and TiO_2 with and without the adsorption of H_2S.

tron donor, could affect the conductivity of TiO_2. The change of the conductivity of TiO_2 upon adsorption of H_2S indicates the strong interaction and the subsequent transfer of charge between TiO_2 and H_2S. Beck and White [10] and Zarifyants et al. [14] reported that the adsorption of H_2S on TiO_2 gives three forms of adsorption states at 1360, 2539 and 2663 cm^{-1}, respectively. The former two are assigned to the bend modes in bound H_2S molecules and H_2S molecules hydrogen-bounded to the surface oxide sites, both of which desorb from the TiO_2 surface at 127°C. The third state is assigned to the bound Ti–SH group. The bound Ti–SH group is irreversibly and strongly adsorbed species, forming at above 327°C. The desorption peak shown in Fig. 1 might be related to two adsorption states at low temperatures. The contribution of these two states to the conductivity of TiO_2 is probably small since the conductivity keeps on increasing with increasing temperature after desorption of these states. Then the major contribution to conductivity might arise from the adsorption of the strongly adsorbed Ti–SH species, which interact more strongly at higher temperatures. With increasing temperature, the S–H bond of strongly adsorbed species becomes weak and finally breaks.

Consequently, H moves to the neighboring oxygen and forms hydroxyl. Because of the electron donation from H, the conductivity is increased. The decline in the conductivity after 200°C, at which the formation of water and sulfur were observed, is due to the formation of H_2O, which results in the following charge transfer or the final insert of S into the oxygen vacancy position.



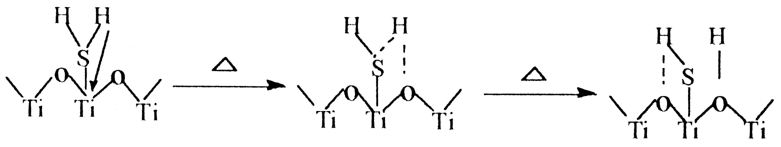
(2)

At temperatures above 300°C, sulfur absorbed on TiO_2 reacts with surface oxygen and forms SO_2, which desorbs from TiO_2 as shown in Fig. 1. Oxygen vacancies are then formed, which is responsible for the increase in conductivity once again. As shown above, because of the semiconductibility and active oxygen on TiO_2 surfaces, the adsorption of H_2S on TiO_2 is rather different in the following two aspects. First, the adsorption of H_2S on TiO_2 is readily converted. At temperatures above 200°C, the adsorbed H_2S reacts with active oxygen in TiO_2 and forms H_2O, S and SO_2. H_2S can also actively interacts with oxygen vacancies and Ti^{3+} in the hydrogen treated TiO_2[H] and releases H_2 while no conversion of H_2S takes place on Al_2O_3. Secondly, the adsorption of H_2S brings about dramatic change of the conductivity of TiO_2, showing a strong interaction between TiO_2 and H_2S. There is not such interaction was observed on Al_2O_3 by TPEC.

3.2. SO_2 adsorption on TiO_2

3.2.1. TPD and IR

The TPD profiles of SO_2 on TiO_2 and Al_2O_3 are shown in Fig. 5. The desorption spectrum of SO_2 on TiO_2 exhibits two overlapping peaks, which illustrates almost complete desorption below 300°C. The desorption of SO_2 on Al_2O_3 again gives a broad desorption peak over a temperature range of 40–500°C. Various adsorption states of SO_2 can be seen from the desorption spectrum on Al_2O_3. Datta et al. [6] investigated



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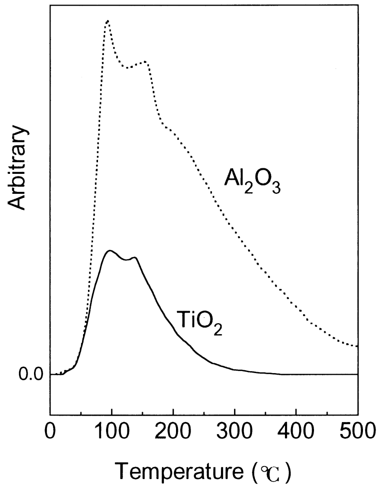


Fig. 5. TPD spectra of SO_2 on TiO_2 and Al_2O_3.

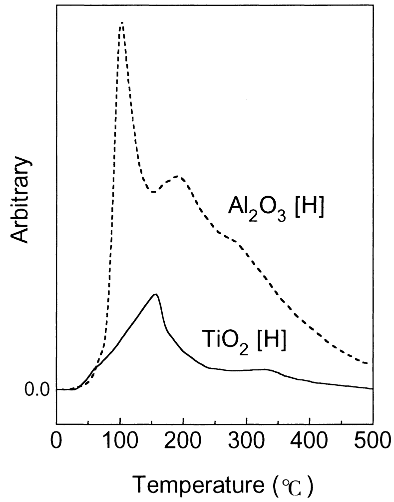


Fig. 6. TPD spectra of SO_2 on the hydrogen pre-treated TiO_2 and Al_2O_3.

the adsorption of SO_2 on Al_2O_3 and reported five different adsorption states of SO_2 on Al_2O_3. Among the five adsorption states, there is a strongly adsorbed state which desorbs at very high temperature.

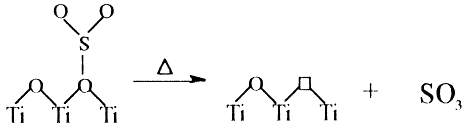
Desorption results in Figs. 1 and 5 show that the adsorption of both H_2S and SO_2 on Al_2O_3 could form some strongly bonded species, which adsorb at active sites on the surface and desorb at high temperatures. This is the main reason why Al_2O_3, as a Claus catalyst, is prone to the sulfation reaction. However, the adsorption of H_2S and SO_2 on TiO_2 cannot form strongly adsorbed states, since the adsorbed states on TiO_2 either desorb easily or transform into different species which can desorb from the surfaces. Therefore, TiO_2 is less vulnerable to the sulfation than Al_2O_3 and keeps active during the Claus reaction [15].

When TiO_2 was hydrogen pre-treated, SO_2 desorption behavior was obviously different from that of the untreated TiO_2 (Fig. 6). The peak at 100°C disappeared, and a new shoulder-like peak appeared at 300°C. During the experiment, the deposition of sulfur on TiO_2 was observed, which indicates the transformation of SO_2 into S. It has been reported that SO_2 could adsorb on Ti^{3+} and form SO_2^- species [16]. TiO_2 treated under H_2 leads to the depletion of surface oxygen ions and the formation of low valence Ti^{3+} for the charge compensation. The partially reduced TiO_2 surface, therefore, is ready to restore the surface structure integrity by accepting suitable atoms such as sulfur ion S^{2-} from SO_2. It is likely that the new desorption peak corresponds to the SO_2^- state on Ti^{3+}. Both H_2S and SO_2 adsorption experiments on the hydrogen-treated TiO_2 demonstrates that TiO_2[H] is more catalytically active to the H_2S and SO_2 adsorbates. Hydrogen treated Al_2O_3 exhibits a similar desorption behavior to untreated Al_2O_3 as shown in Fig. 6.

To further investigate the SO_2 adsorption on TiO_2 and treated TiO_2[H], IR experiments were carried out. Fig. 7 shows the IR spectra of SO_2 adsorption on TiO_2 and TiO_2[H] at various temperatures. Two main adsorption bands at 1280 and 1330 cm^{-1} were observed for both the treated and the untreated TiO_2.

The 1330 cm^{-1} band, assigned to SO_2 adsorbed at surface oxygen sites, is strong on TiO_2, but much weak on TiO_2[H]. The latter band at 1280 cm^{-1}, assigned to SO_2 adsorbed at Ti^{3+} site, is absent on TiO_2 at low temperatures but increases gradually at elevated temperatures. On the contrary, the band at 1280 cm^{-1} on TiO_2[H] is relatively strong and decreases with increasing temperature. According to the above IR information, the adsorption processes of SO_2 on TiO_2 and TiO_2[H] can be rationalized as follows:

On TiO_2 =



(3)

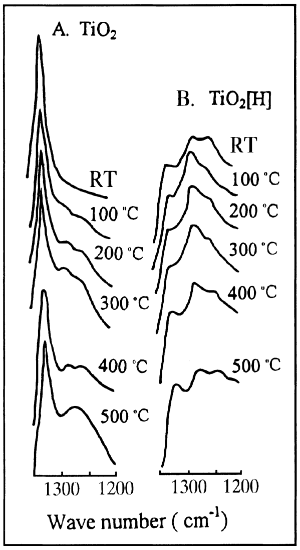
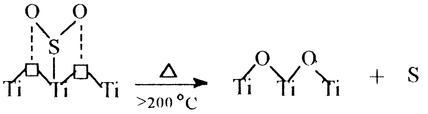


Fig. 7. IR spectra of SO_2 on both TiO_2 and the hydrogen pre-treated TiO_2 after adsorption of SO_2 and treatment at various temperatures.

On $TiO_2[H]$:



(4)

3.2.2. TPEC

The effect of SO_2 adsorption and the subsequent programmed temperature increase on the conductivity of both TiO_2 and $TiO_2[H]$ is shown in Fig. 8. In contrast to the effect of H_2S on the conductivity, the adsorption of SO_2 causes the decrease of the conductivity in TiO_2. The decrease in conductivity of $TiO_2[H]$ is even more severe. SO_2 is an electron acceptor which behaves like O_2. The adsorption of SO_2 on TiO_2 takes place at Ti^{3+} sites and forms SO_2^- [16]. The charge transfer from TiO_2 to the adsorbed SO_2 results in the reduction of conductivity. Examining both TPD in Fig. 5 and TPEC in Fig. 8, several points are worth noting:

(a) In the case of TiO_2, a large proportion of the adsorbed SO_2 contributes little to the conductivity, since the conductivity changes slightly before and after SO_2 desorption at 200°C.

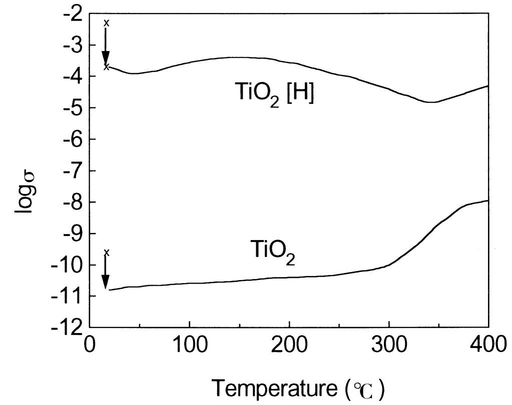


Fig. 8. TPEC profiles of TiO_2 and the hydrogen pre-treated TiO_2 after adsorption of SO_2.

(b) The decrease in conductivity is caused by the adsorption state of SO_2 at higher temperatures. Desorption of this kind of SO_2 leads to the increase in conductivity.

(c) Above 300°C, the further increase in conductivity is probably due to the desorption of SO_2, leaving oxygen vacancies via process(3).

(d) In the case of $TiO_2[H]$, the rapid decrease in conductivity above 200°C occurs when $TiO_2[H]$ takes oxygen from SO_2, filling part of oxygen vacancies via process(4).

(e) When temperature increases to above 300°C, previously formed S is re-oxidized and desorbs from the surface. Thus, the conductivity regains. As demonstrated in TPEC, it is further confirmed that SO_2 adsorbed on TiO_2 and $TiO_2[H]$ can be transformed.

3.3. *Effect of H_2S on SO_2 adsorption on TiO_2*

In the Claus reaction, H_2S and SO_2 are co-fed into the reactor. Therefore, it is of practical importance to investigate the co-adsorption of H_2S and SO_2 on TiO_2. Smith et al. [17] found that the adsorption of SO_2 on untreated TiO_2 is weak, but much stronger on the pre-treated TiO_2 with oxygen vacancies or low valence titanium, Ti^{3+}.

Karge and Dalla Lana [5] reported that the H_2S adsorption on a catalyst under reaction conditions could not be detected by IR spectrometer. While a strongly adsorbed SO_2 state detected by IR could play an important role. Considering that H_2S is more

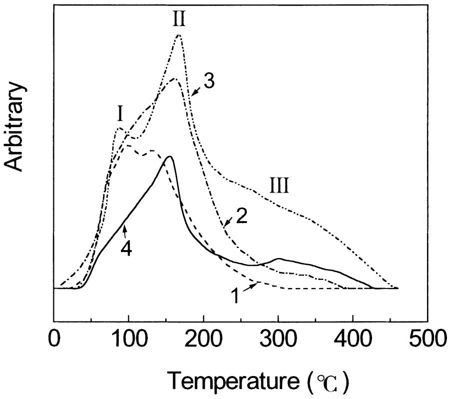


Fig. 9. TPD spectra of SO_2 on TiO_2 pre-treated at various conditions: (1) TiO_2; (2) TiO_2 pre-treated by H_2S for the first time; (3) TiO_2 with 5 times of H_2S treatments; (4) TiO_2[H] pre-treated by hydrogen.

concentrated in the reaction and chemisorptively active on TiO_2, we examined the SO_2 adsorption behavior on TiO_2 pre-treated by H_2S. Fig. 9 shows TPD profiles of SO_2 adsorbed on a H_2S treated TiO_2 as well as on a untreated TiO_2 for comparison. There are two desorption peaks centered at about 100°C and 140°C (curve 1) for the untreated TiO_2. TiO_2 was treated by H_2S pulse for adsorption at room temperature for the first time (curve 2) and several times (curve 3, each time 0.26 ml H_2S injection), Curve 4 is TPD spectrum of SO_2 on the H_2 pre-treated TiO_2. The peak at 100°C is almost unaffected. While the peak at 140°C increases and shifts to higher temperatures and a shoulder peak appears at around 300°C as the number of H_2S treatment increases. The more pronounced change is observed as shown in curve 3 for 5 times H_2S treatments. Similar to H_2 treatment, the treatment by H_2S results in the removal of surface oxygen and the formation of low valence Ti^{3+}. Therefore, SO_2 desorption behavior should resemble that of TiO_2 treated by H_2 (curve 4). It remains unclear why H_2S treatment has a very slight influence on the desorption peak at 100°C, while a pronounced decrease in desorption peak is observed on H_2 treated TiO_2. It might be related to the complicated situation in which sulfur desorption or sulfur insertion into the TiO_2 lattice also occurs. The peak at 100°C corresponds to SO_2 adsorbed at oxygen site on the surface. The peak at 140°C and 300°C are SO_2 adsorbed at the reduced Ti^{3+}. H_2S pre-treatment enhances the SO_2 adsorption on TiO_2 and SO_2 adsorption is significantly affected by the presence of H_2S. Fig. 10 demonstrates the electronic conductivity fluctuation of TiO_2 when H_2S and SO_2 was introduced alternatively at 230°C. It is seen that the electronic conductivity of TiO_2 increases and decreases correspondingly with the adsorption of H_2S and SO_2, indicating electron donation and acceptance between TiO_2 and adsorbates. The scheme of the charge transfer has been postulated earlier [18], which is illustrated below. Under practical Claus reaction conditions, TiO_2 catalyst can be considered serving as a relay for charge transfer between H_2S and SO_2. H_2S adsorbs on TiO_2 and donates electrons to TiO_2. TiO_2 is then partially reduced. Electrons then pass to the adsorbed SO_2 and TiO_2 is re-oxidized.

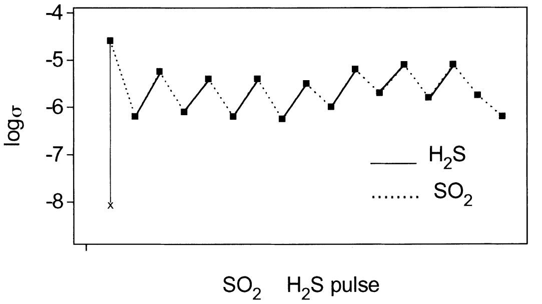
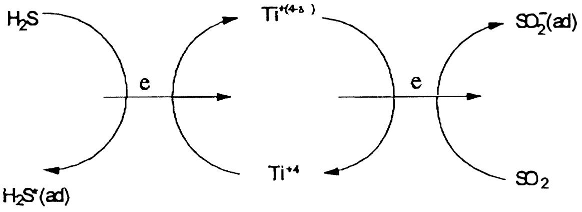


Fig. 10. Variation of Electronic conductivity of TiO_2 as H_2S and SO_2 are introduced alternatively at 230°C.



3.4. Comparison of catalytic performances of TiO_2 and γ-Al_2O_3

In the practical Claus reaction, the following reactions take place on catalysts. A good Claus catalyst should exhibit both high activity and stability toward the following reactions:

$$2H_2S + SO_2 = 3/xS_x + 2H_2O \quad (5)$$

$$CS_2 + H_2O = COS + H_2S \quad (6)$$

Table 1
Comparison of catalytic performances of TiO_2 and γ-Al_2O_3 for the Claus reaction and hydrolysis reaction at 230°C, 5000 h^{-1}

Catalyst	Claus reaction, conversion (%)[a]	CS_2 hydrolysis (%)[b]	CS_2 hydrolysis (%)[c]
TiO_2	96	95	70
γ-Al_2O_3	96	100	30

[a] 3 vol% H_2S, 1.5 vol% SO_2, N_2 balance.

[b] 1 vol% CS_2, 20 vol% H_2O, N_2 balance.

[c] 3 vol% H_2S, 1.5 vol%SO_2, 1 vol% CS_2, 20 vol% H_2O, N_2 balance, results obtained after 14 h.

$$COS + H_2O = H_2S + CO_2 \quad (7)$$

A comparison has been made on the catalytic performances of TiO_2 and γ-Al_2O_3 for the Claus reaction. Table 1 shows the results of the Claus reaction and hydrolysis reaction of CS_2 over TiO_2 and Al_2O_3 at 230°C, 5000 h^{-1}.

Although the conversion of H_2S for the Claus reaction on TiO_2 and γ-Al_2O_3 are both 96% and the conversion of CS_2 hydrolysis reaction on γ-Al_2O_3 is even higher, the conversion of CS_2 hydrolysis reaction in the mixture reactants is much lower on γ-Al_2O_3 than that on TiO_2. Moreover, as shown in Fig. 11, the resistances to the sulfate poison of TiO_2 and γ-Al_2O_3 are remarkably different. H_2S conversion keeps unchanged on TiO_2 catalyst after sulfated for 16 h, while H_2S conversion decreases by 15% on γ-Al_2O_3 sulfated for 10 h. Analysis of SO_4^{2-} on the spent TiO_2 and γ-Al_2O_3 revealed that SO_4^{2-} on the pre-sulfated γ-Al_2O_3 was increased from 0.02 wt% before the test to 3.1 wt%, almost 5 times as high as that on TiO_2. The results show that TiO_2 is much more resistant to the sulfate formation. Accordingly, the effect of pre-sulfation of TiO_2 and γ-Al_2O_3 on the hydrolysis of CS_2 is of significant difference (Fig. 12). After pre-sulfation, the conversion of CS_2 on γ-Al_2O_3 dramatically dropped to almost zero from 100% on the fresh γ-Al_2O_3. Unlike γ-Al_2O_3, TiO_2 showed a rapid recovery of the conversion of CS_2 reaction to 80% although the initial conversion of CS_2 is also close to zero. The comparable results demonstrated that sulfate formed on TiO_2 is unstable and the active sites can be restored under reaction conditions. However, upon the formation of sulfate on γ-Al_2O_3, active sites are occupied and cannot be regenerated.

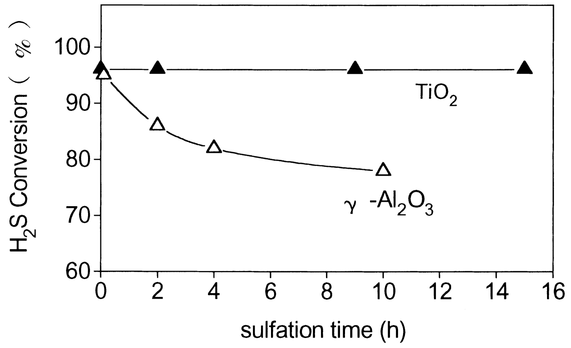


Fig. 11. Effect of pre-sulfation of TiO_2 and γ-Al_2O_3 on H_2S+SO_2 reaction, the same reaction conditions as in Table 1(c). Pre-sulfation was carried out at a air to SO_2 ratio of 7:3, 450°C.

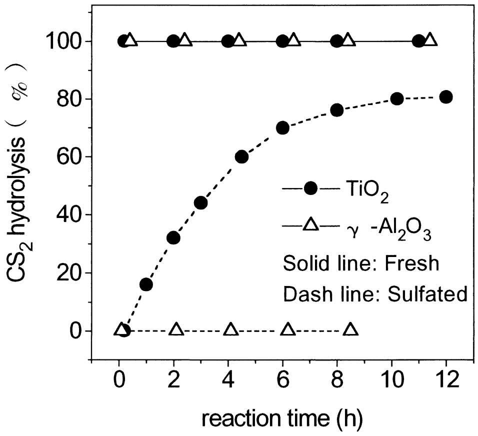


Fig. 12. Effect of pre-sulfation of TiO_2 and γ-Al_2O_3 on the CS_2 hydrolysis reaction, 230°C, 1000 h^{-1}. Pre-sulfation was carried out at a air to SO_2 ratio of 7:3, 450°C for 2 h.

The above results show that although both TiO_2 and γ-Al_2O_3 exhibit high activities for the Claus and hydrolysis reactions, TiO_2 displays a higher resistance to the formation and poisoning of sulfate under reaction conditions.

4. Conclusion

1. Adsorption of H_2S and SO_2 on TiO_2 is quite different from that of Al_2O_3. TiO_2 strongly interacts with H_2S and SO_2, and exchanges charge with the adsorbates, functioning as a charge relay.
2. Above 200°C, lattice oxygen in TiO_2 actively reacts with adsorbed H_2S and SO_2. However,

Al_2O_3 only provides surface adsorption sites, which can be irreversibly occupied by strong adsorption states of H_2S and SO_2. Thus, TiO_2 exhibits superior catalytic properties for the Claus reaction to Al_2O_3.

3. Because TiO_2 is reactive toward H_2S and SO_2 and the desorption of H_2S and SO_2 from TiO_2 can readily takes place, active sites on TiO_2 surfaces is, therefore, difficult to be strongly adsorbed by sulfur oxide or to be irreversibly sulfated.

References

[1] C.C. Chang, J. Catal. 53 (1978) 374.
[2] X.Y. Zheng, Petroleum Natural Gas Chem. Eng. 4 (1984) 45.
[3] D. Thierry, V. Robert, GB 2112597A (1981).
[4] A.V. Deo, I.G. Dalla Lana, J. Catal. 21 (1971) 270.
[5] H.G. Karge, I.G. Dalla Lana, J. Phys. Chem. 88 (1984) 1538.
[6] A. Datta, R.G. Cavell, R.W. Tewer, Z.M. George, J. Phys. Chem. 89 (1985) 443.
[7] R. Fiedorow, I.G. Dalla Lana, S.E. Wanke, J. Phys. Chem. 82 (1978) 2474.
[8] H.G. Karge et al., Proceedings of the Eighth International Congress on Catalysis, Berlin, Germany, 1984, p. 453.
[9] H. Saussey, O. Saur, J.M. White, J. Chim. Phys. Phys-Chim. Biol. 81 (1984) 261.
[10] D.D. Beck, J.M. White, J. Phys. Chem. 90 (1986) 3123.
[11] A. Datta, C.G. Ronald, J. Phys. Chem. 89 (1985) 450.
[12] M. Che, A.J. Tench, Adv. Catal. 32 (1983) 44.
[13] T. Katsumi, K. Tanaka, J.M. White, J. Phys. Chem. 86 (1982) 4708.
[14] Y.A. Zarifyants, S.N. Karyagin, J.E. Kiselev, S.V. Khrstalevo, Kinet Katal. 15 (1974) 1077.
[15] S. Matsuda, A. Kato, Appl. Catal. 8 (1983) 149.
[16] A.I. Mashchenko et al., Kinet Katal. 8 (1967) 704.
[17] K.E. Smith et al., Phys. Rev. B Condnes. Matter 35 (1987) 5822.
[18] W.Z. Li, Y.X. Chen, C.Y. Yu, Proceedings of the Eighth International Congress on Catalysis, Berlin, Germany, 1984, p. 205.