Prevention against catalytic poisoning by H_2S utilizing TiO_2 photocatalyst

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Abstract

Prevention against H_2S-derived catalyst deactivation on Pd catalyst (Pd/TiO_2) was investigated using TiO_2 photocatalytic reaction. The catalytic activity was evaluated by CO oxidation. In the dark, the catalytic activity reduced and completely deactivated in the presence of H_2S. In contrast, under UV light illumination condition, even in the presence of H_2S with the same concentration, it was found that the catalyst kept the activity because of the photocatalytic reaction of TiO_2, resulting in the oxidation of H_2S to sulfate. The completely deactivated catalyst was also regenerated by the photocatalytic reaction.
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1. Introduction

Catalyst deactivation by poisoning is a serious problem in several catalytic reactions [1,2]. Especially, noble metal catalysts are easily deactivated by very small amounts of poisoning species. Therefore, the method of removal of catalyst poisoning or weakening of its effect is extremely important and numerous studies about it have been conducted [3–8]. For example, Twigg and Spencer reported that Cu/ZnO (Cu catalyst was supported by ZnO) improved H_2S resistance due to the removal of H_2S by formation of ZnS [3]. Rodriguez et al. investigated hydrogenation of 1,3-butadiene on Pd/SiO_2 catalyst in the presence of catalytic poisoning gas of H_2S [4]. They represented that the catalyst was deactivated in the presence of H_2S, however the deactivated catalyst was regenerated by reduction of sulfur contaminants, which was adsorbed on it, and desorption of them from it by flowing mixed gases of H_2 and 1,3-butadiene. Maxted investigated the detoxification of artificial hydrogenation systems containing cysteine ($C_3H_7NO_2S$), which worked as a poisonous impu-

rity and reduced the catalytic activity. The catalytic activity was regenerated by the oxidation of cysteine into cysteinic acid by the addition of hydrogen peroxide in the presence of molybdic acid [5]. These studies suggested that the catalysts could be regenerated and their lifetimes could be lengthened by using adsorbent of catalyst poisoning or reduction and oxidation of it.

The present work is focused on a novel method of weakening the toxic effect of H_2S on Pd catalyst by TiO_2 photocatalytic oxidation. The TiO_2 photocatalyst also acts as a support for the Pd catalyst. When the TiO_2 is irradiated with ultraviolet (UV) light, electrons and holes are generated in it. These holes or $^\bullet$OH radicals (formed from the reaction of holes with water molecules adsorbed on the TiO_2 surface) have the strong oxidizing power to decompose organic compounds [9]. The H_2S is oxidized to SO_4^{2-} via SO_2 or SO_3^{2-} by TiO_2 irradiated with UV light [10,11].

Oxidation of CO on Pd/TiO_2 (Pd-deposited TiO_2) was used as a model reaction because it is a simple but an important reaction that is studied extensively both in scientific and practical fields, such as surface science and automotive exhaust control, respectively [12,13]. H_2S was selected as the catalytic poisoning species because it is one of the worst

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and most commonly encountered compounds among sulfur-containing compounds, which make catalysts deactivate.

2. Experimental

2.1. Preparation of catalyst

Pd/TiO$_2$ catalyst was prepared by the photodeposition method [14,15]. Five gram of commercially available anatase-type TiO$_2$ powder (ST-21, Ishihara Sangyo Kaisha Ltd., Japan) with surface area of 50 m^2/g was added into 300 ml of methanol (25 vol.%)–water (75 vol.%) solution containing 0.083 g of PdCl$_2$ (Wako Pure Chemical Industries, Ltd., Japan), and then stirred for 2 h with Ar bubbling to remove the dissolved O$_2$. This solution was then irradiated with UV light for 1 day to reduce Pd$^{(2+)}$ to Pd$^{(0)}$. This powder was filtered up, washed thoroughly with deionised distilled water, and dried in air at 393 K for 5 h, resulting in the Pd/TiO$_2$ catalyst with a nominal Pd content of 1 wt.%. Obtained powder was irradiated with UV light for 1 day to remove organic impurities.

2.2. Measurement

Reaction tests were carried out in a static batch system. A powder of 0.1 g prepared sample, spread uniformly over a 5.7 cm^2 area, was set in a batch-type reactor of a closed glass vessel with volume of 500 ml. Then 30 ppm of CO or a mixture of 30 ppm of CO and 100 ppm of H$_2$S in synthetic air was introduced into the vessel every 1 h. UV light with intensity of 10 mW/cm^2 was irradiated by an Xe–Hg lamp at room temperature. The UV light intensity was controlled by a UV radiometer (UVR-2, UD-36, Topcon Corp., Japan). The CO and CO$_2$ concentrations were measured utilizing a gas chromatograph (GC-8A, Shimadzu Corp., Japan) equipped with a flame ionization detector–methanizer. H$_2$S and SO$_2$ were measured utilizing a gas chromatograph (GC-8A, Shimadzu) equipped with a flame photometric detector. Surface sulfur states were analyzed by X-ray photoelectron spectroscope (XPS, PHI-5600, ULVAC-PHI Inc., Japan) with un-monochromatized X-rays (Mg Kα). The binding energy was calibrated by the C 1s spectrum at 284.5 eV. We repeated all experiments for three times. The coefficients of repeatability for three runs were less than 3%.

3. Results and discussion

3.1. Catalytic activity of Pd/TiO$_2$ in the absence of H$_2$S

Fig. 1 shows the concentration change of CO and CO$_2$ with reaction time in the absence of H$_2$S in the dark (without UV light illumination). The CO concentration in the gas phase decreased with increasing in the reaction time, and became undetectable in about 1 h. CO oxidation resulted in
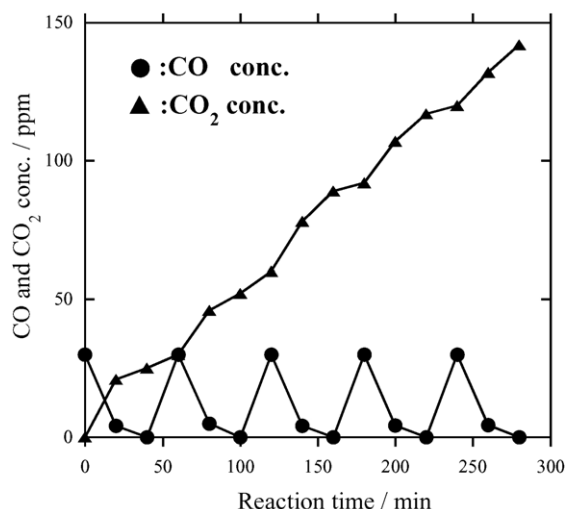

Fig. 1. Time dependence of CO oxidation into CO$_2$ in the absence of H$_2$S on Pd/TiO$_2$ in the dark. Thirty parts per million of CO was injected into the vessel every 1 h.

the increase of CO$_2$ concentration, as is shown clearly in Fig. 1. After 280 min, the CO$_2$ concentration reached about 150 ppm, which was equal to the total amount of injected CO. This result indicates that CO was completely oxidized into CO$_2$ on Pd surface under the present experimental condition. Catalyst deactivation was not observed at all, even after fifth cycle of CO oxidation, revealing that CO and CO$_2$ do not work as catalytic poisoning species on the Pd/TiO$_2$ catalyst.

3.2. Catalytic activity of Pd/TiO$_2$ in the presence of H$_2$S

Figs. 2 and 3 show the catalytic activity of CO elimination on Pd/TiO$_2$ in the presence of H$_2$S in the dark and under UV light illumination, respectively. Performance of the CO conversion decreased with increasing in the total amount of
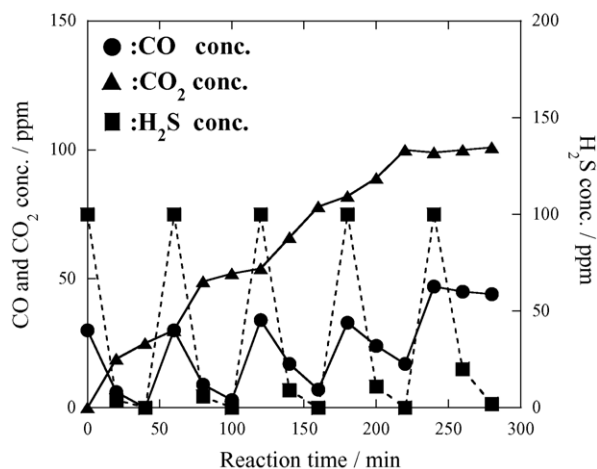

Fig. 2. Time dependence of CO oxidation into CO$_2$ in the presence of H$_2$S on Pd/TiO$_2$ in the dark. Thirty parts per million of CO and 100 ppm of H$_2$S were injected into the vessel every 1 h.
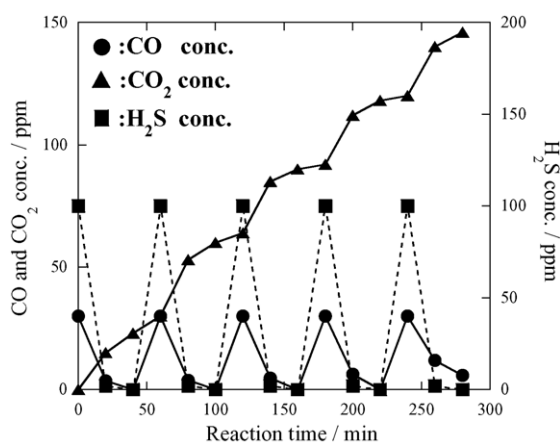
Fig. 3. Time dependence of CO oxidation in the presence of H_2S on Pd/TiO_2 under UV illumination. Thirty parts per million of CO and 100 ppm of H_2S were injected into the vessel every 1 h.

H_2S injected, as is shown in Fig. 2. After fifth cycle of CO and H_2S injection, the catalyst became completely deactivated, as demonstrating only a slight decrease of CO and no increase in CO_2 production. The H_2S was not detected in the gas phase at the reaction time of 280 min. It was considered that H_2S was adsorbed on catalyst surface and it worked as catalytic poisoning species. However, when UV light was illuminated on the catalyst, a remarkable difference in the catalytic behavior was observed, as is shown in Fig. 3. Compared with the case without UV light illumination (Fig. 2), the catalytic activity was improved greatly by UV light illumination. The catalyst under UV light illumination was still efficiently active in 280 min, whereas the catalyst has become deactivated at the same reaction time without UV light illumination. To comprehend the activity further, similar experiments were carried out over Pd supported by Al_2O_3, which is not a photocatalyst. In the presence of H_2S, the catalyst was completely deactivated after fifth cycle of H_2S introduction in the dark or under UV light irradiation. The lifetime in the dark was as same as that under UV light irradiation. No improvement of the activity was seen by UV light irradiation on Pd and support (Al_2O_3).

In the dark, CO was oxidized into CO_2 on only Pd surface, however under UV light illumination, CO oxidation is also expected to proceed on the TiO_2 surface by photocatalytic reaction [16,17], as well as on the Pd surface. To estimate the contribution of the photocatalytic reaction to CO oxidation, we evaluated the initial rate of CO elimination in 20 min. The rates in the dark in the absence of H_2S (Fig. 1), in the dark in the presence of H_2S (Fig. 2) and under UV illumination in the presence of H_2S (Fig. 3) were estimated to be 1.3, 1.2 and 1.3 ppm/min, respectively, and the rates were almost same. It was suggested that the CO oxidation rate on the Pd surface is much larger than that on TiO_2 by the photocatalytic reaction and that CO oxidation took place mainly on the Pd surface rather than TiO_2 surface even under UV light illumination. These results agree with the previous study [18].

Einaga et al. compared adsorption and oxidation properties of CO on TiO_2 with Pt (1 wt.%)/TiO_2. They reported that the rate for CO photocatalytic oxidation on Pt/TiO_2 was higher than that on TiO_2 in the presence of water vapor and that the CO was hardly oxidized on TiO_2 surface under UV illumination. They concluded by FT-IR studies that CO was more efficiently adsorbed on Pt compared with TiO_2 and Pt acted as the active sites on which CO was oxidized to CO_2 on photoirradiation.

In contrast, it was suggested that part of adsorbed and gaseous H_2S was oxidized and the poisoning effect decreased by photocatalytic reaction, resulting in keeping its activity. SO_2, an intermediate of the H_2S photocatalytic oxidation, was not detectable in the gas phase during light illumination. It was indicated that even if SO_2 was produced, SO_2 was not desorbed from the catalyst and the amount of catalyst poisoning species on it did not change.

3.3. Reactivation

Reactivation treatments by illumination with UV light were applied to the completely deactivated sample after reaction time of 280 min, in Fig. 2. The deactivated sample was irradiated with UV light for 0, 69 and 100 h. The elimination activity of CO for this treated sample was evaluated in the dark condition, as is shown in Fig. 4. For comparison, the activity for as-prepared sample (i.e. the first cycle of CO elimination in Fig. 1) is also shown in Fig. 4. These results indicated that the completely deactivated catalyst could be regenerated by UV illumination and the activity of CO elimination increased with increase in the illumination time of UV light. Even after the UV light illumination of 100 h, its activity was inferior to that of as-prepared catalyst. The reason for it will be discussed later.
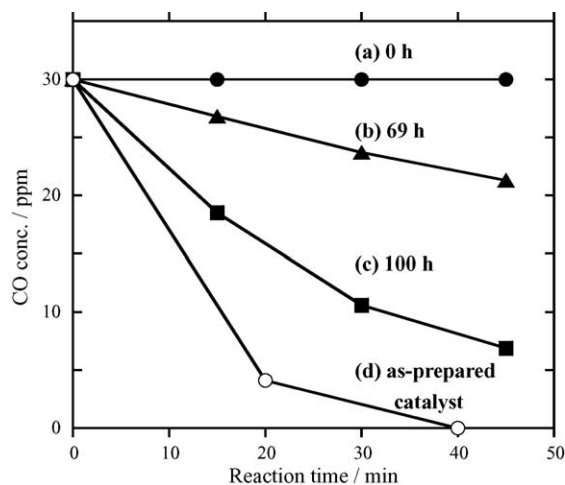

Fig. 4. Influence of the time of reactivation treatment by UV light illumination on the activity. (a) Deactivated sample without illumination; (b) regenerated sample after 69 h illumination; (c) regenerated sample after 100 h illumination; (d) as-prepared catalyst.
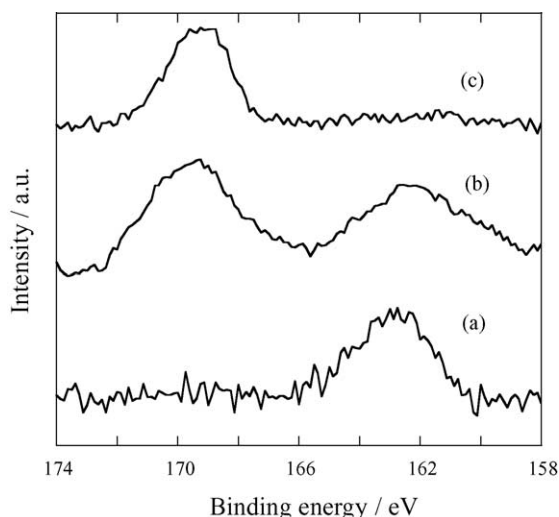
Fig. 5. XPS spectra of S 2p on the surface of deactivated and regenerated catalysts. (a) Sample at 280 min in Fig. 2; (b) sample at 280 min in Fig. 3; (c) regenerated sample after 100 h illumination in Fig. 4.

3.4. Surface characterization

Fig. 5 shows the XPS spectra of S 2p on the poisoned and regenerated catalyst surface. The spectrum (a), measured on the surface of the completely deactivated catalyst after illumination time of 280 min in Fig. 2, had one peak observed at binding energy of 163 eV and this peak corresponded to sulfide compounds [19–22]. It was suggested that H_2S which had been adsorbed on the catalyst (mainly on the Pd surface) caused the decrease in the catalyst activity. The spectrum (b), measured on the surface of the active catalyst after the illumination time of 280 min in Fig. 3, had two main peaks, corresponding to sulfide compounds (H_2S, 163 eV) and sulfate compounds (SO_4^{2-}, 169 eV). The peak at 169 eV in the spectrum (b) had a shoulder at around 167 eV, corresponding to SO_2 or SO_3^{2-}, compared with that at 169 eV in the spectrum (c) [19–22]. These results indicated that part of adsorbed and gaseous H_2S was oxidized into sulfate via SO_2 or SO_3^{2-}. The spectrum (c) of the regenerated catalyst in Fig. 4 had one peak corresponding to sulfate. Therefore, it was confirmed that the UV light illumination could convert the sulfide to the sulfate. This conversion is attributable to the oxidation of H_2S by TiO_2 photocatalytic reaction [10]. Maxted has reported that the poisoning effect of sulfate was less than that of sulfide by comparing the catalytic poisoning of sulfur containing compounds [5]. Sulfide compounds are coordinated directly with Pd using two anti-bonding lone pairs. The activity of Pd catalyst was reduced drastically by sulfide. In contrast, the sulfur atom of sulfate is surrounded by oxygen atoms. The structure of sulfate satisfies with the octet rule and the sulfur atom of sulfate does not bind directly with Pd. The interaction between Pd and S atom of sulfate is smaller than that of sulfide, and thus the poisoning effect of sulfate is smaller [5]. The catalyst supported by TiO_2 photocatalyst with UV light illumination is considered to prevent

the catalyst deactivation due to the conversion of H_2S to the sulfate. Although the sulfate is less poisonous, it is a kind of catalytic poisonous species. Therefore, the activity of CO elimination by the 100 h-UV light illumination sample was inferior to that of the as-prepared catalyst in Fig. 4.

The generated sulfate on the TiO_2 surface is easily removed by washing the regenerated sample with distilled water [10,23]. It is expected that the catalyst will be more reactive, possessing a similar level to activity of the as-prepared catalyst, by washing with distilled water. It is anticipated that the Pd and TiO_2 combination with the UV light treatment is the promising method of preventing against the catalytic poisoning originated from H_2S.

4. Summary

A novel method of preventing catalytic poisoning by H_2S was suggested. Pd-deposited TiO_2 catalyst showed enhanced activity of CO to CO_2 conversion in the presence of H_2S under illumination with UV light, compared to that in the dark. This is because the TiO_2 irradiated with UV light could oxidize H_2S to sulfate, which is less poisonous than H_2S. Although produced sulfate remained on the surface of the catalyst, it can be easily removed by distilled water. Our proposal in the present study is considered to be a promising method of preventing against the H_2S-derived catalytic poisoning. In addition, this method is expected to apply to prevent the catalyst poisoning not only by sulfur containing compounds but also by other non-metallic compounds.

References

[1] J.P. Franck, G.P. Martino, in: J. Oudar, H. Wise (Eds.), Deactivation and Poisoning of Catalysis, Marcel Dekker, Inc., New York, 1985, p. 205.
[2] M. Shelef, K. Otto, N.C. Otto, Adv. Catal. 27 (1978) 311.
[3] M.V. Twigg, M.S. Spencer, Appl. Catal. A 212 (2001) 161.
[4] J.C. Rodriguez, J. Santamaria, A. Monzon, Appl. Catal. A 165 (1997) 147.
[5] E.B. Maxted, Adv. Catal. 3 (1951) 129.
[6] L.J. Hoyos, M. Primet, H. Praliaud, J. Chem. Soc. Faraday Trans. 88 (1992) 113.
[7] C. Nicot, R. Frety, Catal. Lett. 38 (1996) 171.
[8] J. Oudar, S. Pinol, C.M. Pradier, Y. Berthier, J. Catal. 107 (1987) 445.
[9] A. Mills, S.L. Hunte, J. Photochem. Photobiol. A 108 (1987) 1.
[10] M.C. Canela, R.M. Alberici, W.F. Jardim, J. Photochem. Photobiol. A 112 (1998) 73.
[11] Y. Matsumoto, H. Nagai, E.-I. Sato, J. Phys. Chem. 86 (1982) 4664.
[12] H. Muraki, H. Shinjoh, H. Sobukawa, K. Yokota, Y. Fujitani, Ind. Eng. Chem. Prod. Res. Dev. 25 (1986) 202.
[13] E.M. Stuve, R.J. Madix, Surf. Sci. 146 (1984) 155.
[14] T. Sano, S. Kutsuna, N. Negishi, K. Takeuchi, J. Mol. Catal. A 189 (2002) 263.
[15] A.V. Vorontsov, I.V. Stoyanova, D.V. Kozlov, V.I. Simagina, E.N. Savinov, J. Catal. 189 (2000) 360.
[16] A. Linsebigler, C. Rusu, J.T. Yates Jr., J. Am. Chem. Soc. 118 (1996) 5284.

[17] S. Sato, T. Kadowaki, J. Catal. 106 (1987) 295.

[18] H. Einaga, M. Harada, S. Futamura, T. Ibusuki, J. Phys. Chem. B 107 (2003) 9290.

[19] T.C. Bromfield, N.J. Coville, Appl. Surf. Sci. 119 (1997) 19.

[20] H. Aono, M. Sakamoto, Y. Sadaoka, J. Ceram. Soc. Jpn. 108 (2000) 1052.

[21] E. Laurent, B. Delmon, J. Catal. 146 (1994) 281.

[22] J.F. Moulder, W.F. Stickle, P.E. Sobol, K.D. Bomben, Handbook of X-Ray Photoelectron Spectroscopy, Perkin Elmer, Corp., USA, 1992.

[23] J. Shang, Y.F. Zhu, Y.G. Du, Z. Xu, J. Solid State Chem. 166 (2002) 395.