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Effect of Calcination Temperature on the Characteristics of SO_4^{2-}/TiO_2 Catalysts for the Reduction of NO by NH_3

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Abstract−The catalytic activity of sulfated titania (ST) calcined at a variety of temperatures has been investigated for selective catalytic reduction (SCR) of NO by NH_3. The NO removal activity of ST catalyst mainly depends on its sulfur content, indicating critical role of sulfur species on the surface of TiO_2. The role of sulfur is mainly the formation of acid sites on the catalyst surface. The presence of both Brønsted and Lewis acid sites on the surface of sulfated titania has been identified by IR study with the adsorption of NH_3 and pyridine on ST. The reduction of the intensity of IR bands representing Brønsted acid sites is more pronounced than that revealing Lewis acid sites as the calcination temperature increases. It has been further clarified by IR study of ST500 catalyst evacuated at a variety of temperatures. The NO removal activity also decreases with the increase of the catalyst calcination temperature. It simply reveals that Brønsted acid sites induced by sulfate on the catalyst surface are primarily responsible for the enhancement of catalytic activity of ST catalyst containing sulfur for NO reduction by NH_3.

Key words: Sulfated Titania (ST), Brønsted Acid, Lewis Acid, Nitric Oxide, SCR

INTRODUCTION

Metal oxide catalyst containing sulfate ion (SO_4^{2-}) has attracted a great deal of attention due to higher catalytic activity for a variety of industrial catalytic processes such as isomerization, alkylation, and cracking [Yamaguchi, 1990; Hino and Arata, 1980; Song and Sayari, 1996]. Sulfated metal oxides have been prepared by treating metal oxides with sulfur compounds such as SO_2, H_2S and $(NH_4)_2SO_4$ under an oxidizing atmosphere [Ebitani et al., 1993; Sayari and Dicko, 1994]. In addition, the solid acid catalyst containing sulfur on its surface may also resolve the environmental problems caused by using a liquid phase sulfuric acid as an acid catalyst.

Titania has been widely employed as a support for a commercial SCR catalyst on which the active species, V_2O_5, WO_3 and/or MoO_3 are well dispersed [Amiridis et al., 1996; Orsenigo et al., 1998; Jung and Grange, 2000a, b]. Titania itself also showed significant NO removal activity and high selectivity to N_2 at a reaction temperature over 400 °C [Alemany et al., 1996]. It has been recognized that the sulfate species on the surface of TiO_2 is favorable for NO removal reaction [Amiridis et al., 1996; Jung and Grange, 2000a]. The sulfate species on the surface of titania affects not only the surface structure of active species but also the catalyst acidity which plays a critical role for deNO$_x$ SCR reaction [Choo et al., 2000a].

However, there is still controversy on which of two types of acid sites on the surface of acidic catalyst, Brønsted and Lewis, is responsible for NO removal activity. Chen and Yang reported that SO_4^{2-}/TiO_2 catalyst prepared by sulfating a sulfur-free TiO_2 (P25) with SO_2 under air atmosphere was highly active for NO reduction reaction by NH_3 over 350 °C [Chen and Yang, 1993]. They suggested that the Brønsted acid sites played an important role for NO removal activity. Jung and Grange recently examined a reaction intermediate during NO reduction by NH_3 over a sulfated TiO_2 by *in situ* DRIFT and NH_3-TPD studies [Jung and Grange, 2000b]. They reported that the Lewis acid site on the surface of sulfated TiO_2 catalyst was responsible for the adsorption of NH_3 reacting with adsorbed NO_3^- by Langmuir-Hinshelwood route, and the reaction rate of NO removal on sulfated TiO_2 catalyst depended on the amount of Lewis acid sites on the catalyst surface.

The purpose of present study is to identify the role of acid sites on the surface of ST catalyst for NO removal activity to clarify their participation to SCR reaction. In particular, which one of two kinds of acid sites, Brønsted and Lewis acid, is responsible for SCR reaction by NH_3, has been discussed to elucidate the role of acid sites. The acidic property including the nature, amount, and strength of acid sites on the surface of sulfated titania has been characterized by FT-IR spectroscopy study with the adsorption of NH_3 and pyridine on sulfated titania. The alteration of the surface acidity on the catalyst surface has been accomplished by controlling the calcination temperature of the catalyst in order to identify the participation of acid sites to NO removal reaction.

EXPERIMENTAL

A series of sulfated titania (ST) was prepared by calcining a metatitainc acid ($TiO(OH)_2$) at a variety of temperatures from 500 to 900 °C [Choo et al., 2000a]. Since the metatitanic acid is a reaction intermediate obtained from the manufacturer of TiO_2 for pig-

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[‡] This paper is dedicated to Professor Baik-Hyon Ha on the occasion of his retirement from Hanyang University.

Table 1. BET surface areas and sulfur contents of the ST catalysts with respect to calcination temperature

Temperature (°C)	Sulfur content (wt%)	S_{BET} (m^2/g)
120	2.29	223
500	1.81	98
600	1.46	77
700	0.24	32
800	0.03	9
900	0	5

ment by sulfate route and exists in a slurry form, it should be dried and calcined at an appropriate temperature in order to prepare solid state TiO_2 and contains sulfur on its surface during the manufacturing process. No extra sulfur was added to the surface of ST catalyst prepared in the present study. The sulfated titania was dried again at 120 °C in air atmosphere overnight and then calcined at a temperature from 500 to 900 °C for 5 h. The sulfur content of the prepared catalyst was measured by LECO SC-132 Sulfur System (LECO Co.). The BET surface area of the catalyst was examined by Micromeritics Accusorb 2100E using N_2 at 77 K. Prior to the measurement of BET surface area, the catalyst was pretreated under vacuum at 150 °C for 12 h. The sulfur content and BET surface area of the prepared catalyst are summarized in Table 1. The number in the catalyst name denotes the temperature at which the calcination has been done.

The NO removal activity of ST catalyst containing a variety of sulfur contents and surface areas by NH_3 was examined in a tubular downstream flow reactor system operated under isothermal and atmosphere pressure condition. Details of the reaction conditions are described in previous studies [Choo et al., 2000a; Ham et al., 2000]. Typical gas composition of feed stream for activity test was 500 ppm NO, 500 ppm NH_3, 5% O_2 and balance N_2. The reactor space velocity based on the ratio of the total gas flow rate to the volume of the catalyst bed was 100,000 h^{-1}. The concentration of NO was measured by on-line chemiluminescence NO-NO_2 analyzer (Thermo Electron, Model 42C).

An infrared study was performed for a self-supporting disk of catalyst with a Perkin-Elmer 1800 FT-IR spectrometer. The disk of catalyst containing a loading of 20-30 mg cm^{-2} was prepared by compressing a catalyst powder under 5×10^3 kg cm^{-2} pressure. The IR cell system consists of two parts: CaF_2 window to take IR spectra in the transmission mode and the sample treatment unit. It is connected to a flow system for sample treatment and transferred to the spectrometer in an in-situ mode without exposing the sample to the atmosphere. Prior to the adsorption of probe gases, the sample was pretreated under oxidizing condition at 400 °C for 1 h. The adsorption of NH_3 or pyridine was performed by flowing the adsorbates into the system for 5 min. To examine the strength of acid sites, IR measurements were performed for the catalyst adsorbing NH_3 evacuated under the flow of He gas at elevated temperatures up to 400 °C for 0.5 h.

RESULTS AND DISCUSSION

1. Effect of Calcination Temperature on NO Removal Activity of ST Catalyst

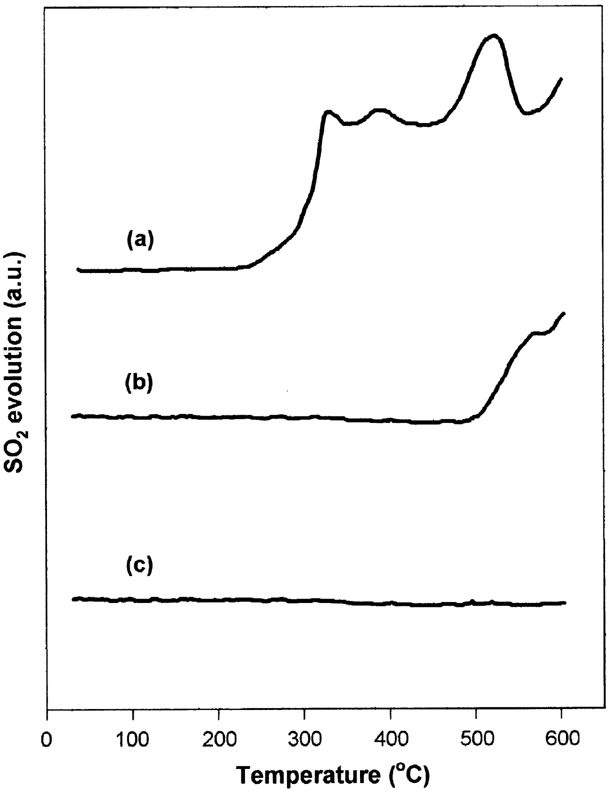

Fig. 1. SO_2 desorption profiles of ST catalyst (a) fresh ST, (b) ST calcined at 500 °C for 5 h, and (c) ST calcined at 800 °C for 5 h.

The alteration of physicochemical properties of sulfated titania (ST) including BET surface area and sulfur contents by calcination temperature from 500 to 900 °C is listed in Table 1. The BET surface area of ST proportionally decreases as the calcination temperature increases. This is mainly due to the sintering of TiO_2 itself during the course of the calcination. The sulfur content on the surface of ST also decreases with the increase of the temperature, and negligible sulfur can be observed on the surface of the catalyst calcined even from 700 °C. Since the reduction of sulfur content is mainly due to the decomposition of sulfur species on the catalyst surface at high calcination temperature, the thermal stability of sulfur species on the surface of ST was examined by temperature programmed desorption (TPD) of SO_2 as shown in Fig. 1.

Since the sulfur species on the catalyst surface are mostly desorbed in a form of SO_2 molecule confirmed by on-line mass spectroscopy from the surface of TiO_2, the evolution pattern of SO_2 has been particularly observed in Fig. 1. The distribution of sulfur species on the surface of ST varies with respect to the calcination temperature of the catalyst. For ST dried at 120 °C, SO_2 begins to evolve from 250 °C and reveals four peaks at 330, 390, 525, and 600 °C. However, SO_2 from ST calcined at elevated temperatures, 500 and 800 °C, evolves just from its calcination temperature. No SO_2 from ST800 has been detected in the downstream of TPD apparatus. The sulfur content on the catalyst surface of ST catalyst can be adjusted by controlling the calcination temperature of the catalyst.

Fig. 2 shows NO removal activity of ST calcined at a variety of temperatures from 500 to 900 °C. NO removal activity has been

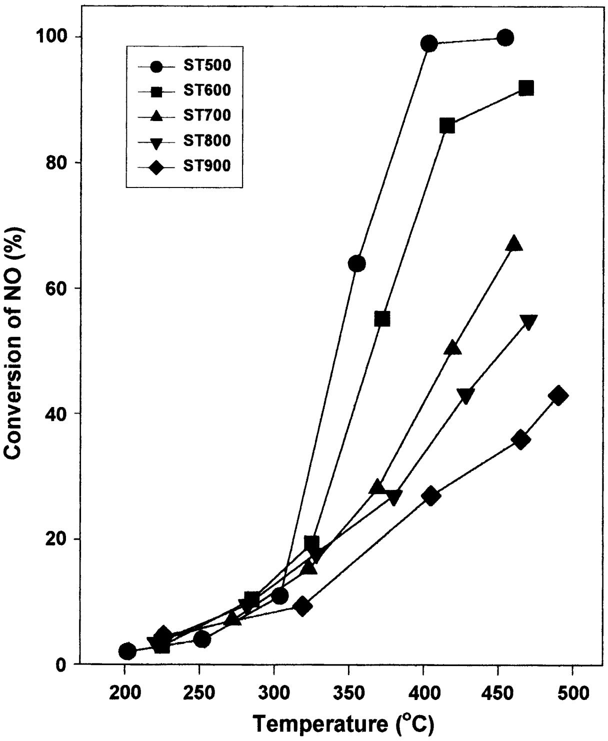

Fig. 2. NO removal activity of ST catalyst; Reactor space velocity= 100,000/h, [NH$_3$]/[NO]=1.0, [O$_2$]=5% in N$_2$.

examined up to the reaction temperature of 500 °C to avoid the further decomposition of sulfur on the catalyst surface. The catalyst reveals a negligible catalytic activity at a reaction temperature below 300 °C, and the activity was strongly influenced by calcination temperature. The catalytic activity increases as the calcination temperature decreases. ST calcined at lower temperature contains a larger amount of sulfur than that calcined at higher temperature. It simply indicates that the NO removal activity of ST primarily depends on the sulfur content. In addition, the decrease of NO removal activity of ST with the increase of calcination temperature may also be attributed to the reduction of surface area. However, it has been well known that the number of Brønsted acid sites increases when sulfur exists on the catalyst surface, which results in an enhancement of NO removal activity by NH$_3$ [Choo et al., 2000a; Ham and Nam, 2002]. This reflects that the acid site generated from the sulfate on the surface of TiO$_2$ plays an important role for SCR reaction to remove NO by NH$_3$ [Choi et al., 1996].

2. Acid Sites on ST Catalyst

In order to investigate the effect of calcination temperature on the surface property of ST catalyst, an infrared spectroscopy study has been accomplished in the present study. Infrared spectra of ST catalyst calcined at a variety of temperatures can be observed in Fig. 3. Not only the spectra for surface sulfate species (1,400-1,200 cm^{-1}), but also the hydroxyl stretching bands (3,800-3,500 cm^{-1}) are mainly examined to investigate the alteration of surface property by the calcination at elevated temperatures.

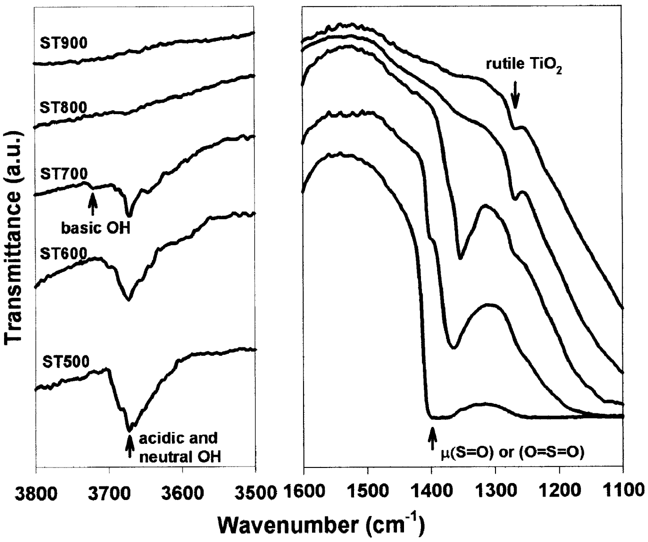

Fig. 3. IR spectra of ST catalyst.

A very intense band can be observed in the region of 1,400 cm^{-1} of IR wavenumber, which is due to the ν(S=O) species of surface $(TiO)_3S=O$ compound [Nortier et al., 1990] and/or to the asymmeric O=S=O stretching species of $(TiO)_2SO_2$ [Navarrete et al., 1996]. In general, the structure of sulfur on the surface of metal oxide alters from isolated species to polynuclear species with the increase of the sulfur content on the catalyst surface. As the calcination temperature increases, the intensity of the IR band at 1,400 cm^{-1} has been reduced and the band shifts to the lower wavenumber of 1,350 cm^{-1}. Above 800 °C, especially, the IR band corresponding to sulfur species disappeared, indicating their complete decomposition on the surface of TiO$_2$. The appearance of IR spectra at 1,270-1,260 cm^{-1} indicates the phase transformation of titania from anatase to rutile due to the high calcination temperature.

It is well known that the IR bands for acidic and neutral hydroxyl groups appear in the region of the wavenumber from 3,700 to 3,600 cm^{-1}, whereas the hydroxyl group at 3,720 cm^{-1} is commonly assigned to the basic hydroxyl group [Pasel et al., 2000; Kustov et al., 1994]. The ST catalysts calcined at 500 and 600 °C do not reveal the band for basic hydroxyl group at 3,720 cm^{-1}. This may be due to the preoccupation of basic sites by sulfur species on the catalyst surface. However, a weak basic hydroxyl group at 3,720 cm^{-1} can be observed on ST700 calcined at 700 °C due to the decomposition of sulfur species on the catalyst surface. The intensity of the hydroxyl groups appearing at 3,670 cm^{-1} was gradually reduced and it completely disappeared for the catalyst calcined at 800 °C. This simply indicates the decrease of the amount of the hydroxyl groups on the surface of ST due to the simultaneous reduction of the catalyst sulfur content and surface area caused by the calcination of ST catalyst.

The acidic property of SCR catalyst plays a critical role for the catalytic performance for NO removal by NH$_3$ [Chen and Yang, 1993; Amiridis et al., 1996; Choi et al., 1996; Jung and Grange, 2000a]. To examine the nature of acidic sites on sulfated TiO$_2$, the infrared spectra of ST catalyst adsorbing pyridine as a probe molecule have been recorded with respect to the calcination temperature as shown in Fig. 4. The IR spectra for a self-supporting TiO$_2$ adsorbing pyridine have been examined at room temperature after pretreatment at 500 °C for 0.5 h in air atmosphere.

Many reports discuss the assignment of the peaks in the infrared spectra for TiO$_2$ adsorbing pyridine [Primet et al., 1971; Busca et

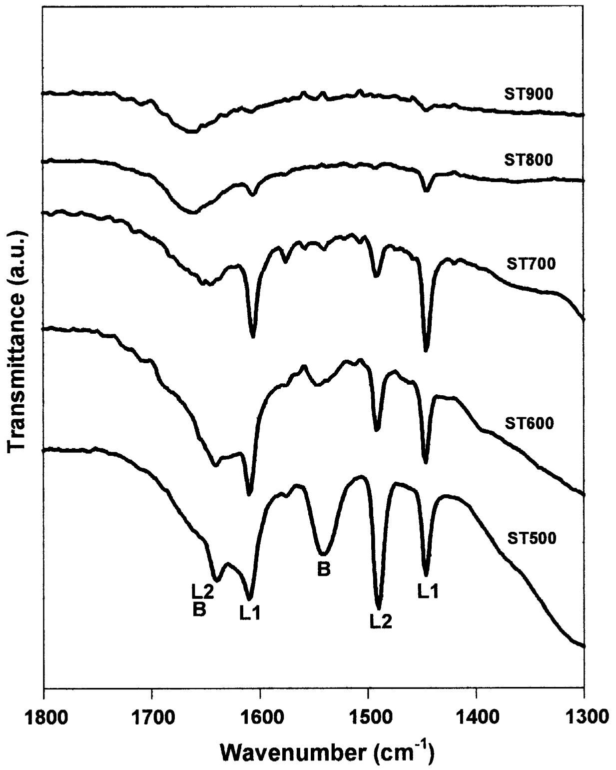

Fig. 4. IR spectra of ST catalyst adsorbing pyridine as a probe molecule.

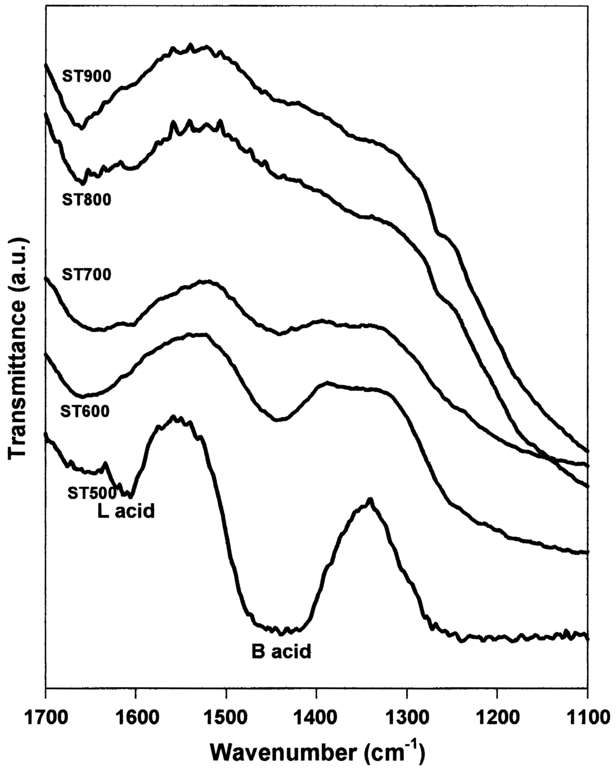

Fig. 5. IR spectra of ST catalyst adsorbing NH_3 as a probe molecule.

al., 1985; Ferwerda et al., 1996]. The ST calcined at 500 °C (ST500) exhibits three characteristic IR bands for pyridine species adsorbed on Lewis acid sites at wavenumbers of 1,444 and 1,607 cm^{-1} (designated as L1 in Fig. 4), of 1,459 and 1,630 cm^{-1} (designated as L2) and Brønsted acid sites at 1,542 and 1,638 cm^{-1} (designated as B). The intensities of the latter two sites, L2 and B, are significantly reduced, while that of L1 has been hardly altered as the calcination temperature of the catalyst increases. Therefore, B and L2 sites are obviously related to the sulfur content on the catalyst surface, since their IR intensities and sulfur contents simultaneously decrease with respect to the calcination temperature. It should be noted that the sudden decrease of the intensity of L1 site for ST calcined at the temperature higher than 700 °C is mainly due to the decrease of the catalyst surface area down to 5 m^2/g. It has been observed that the alteration of IR intensity for B sites is more pronounced than that for L2 sites with respect to the calcination temperature. Indeed, the formation of Brønsted sites on the catalyst surface is strongly influenced by the dehydration of the catalyst including the calcination of the catalyst [Ward, 1976].

Additionally, the surface acidity of ST catalyst adsorbing NH_3 as a probe molecule has been also examined by infrared spectroscopy. The adsorption of NH_3 on the surface of TiO_2 is important for understanding the reaction of the SCR system, since NH_3 is one of the major reactants for SCR reaction as well as a probe molecule for the measurement of the surface acidity. Fig. 5 shows IR spectra of ST adsorbing NH_3 observed at room temperature. Two major bands can be observed at the wavenumber of 1,610 and 1,450 cm^{-1} corresponding to Lewis (L) and Brønsted (B) acid sites, respectively [Tanabe, 1970]. The intensity for Brønsted acid site has been apparently reduced, whereas that for Lewis acid sites is gradually decreased probably due to the decrease of the surface area upon the catalyst calcination. The degree of the alteration for the intensity of IR band for both sites is distinctive, which is quite similar to the trend observed for ST adsorbing pyridine as shown in Fig. 4. However, the participation of Lewis acid sites to SCR reaction cannot be eliminated, since the intensity of the IR band at 1,610 cm^{-1} for ST catalyst also gradually decreased with respect to the calcination temperature of the catalyst. It has been observed that the NO removal activity of ST catalyst with respect to calcination temperature, as shown in Fig. 2, correlates well with the decrease of the intensity for Brønsted acid sites on the catalyst surface. Note that the intensity of IR in transmission mode may indicate the amount of the corresponding acid sites on the catalyst surface.

The contribution of Brønsted (B) acid sites to SCR reaction on ST catalyst prepared in the present study becomes evident by the study controlling the evacuation temperature of NH_3 from acid sites on the surface of a given catalyst, ST500 adsorbing NH_3 as shown in Fig. 6. It can eliminate the contribution of the decrease of the catalyst surface area to the reduction of IR intensity of both acidic sites which could not be clarified in Figs. 4 and 5. Note that this technique has been commonly employed for measuring the strength of the acid sites on the catalyst surface. Prior to IR measurement at room temperature, ST500 catalyst was exposed to NH_3 and followed by the evacuation at a variety of temperatures in the range from 150 to 400 °C. It may also suggest the possibility of the participation of Lewis acid sites to SCR reaction which was suspected for the IR study in Fig. 5.

The IR spectra of ST500 adsorbing NH_3 in Fig. 6 contains two

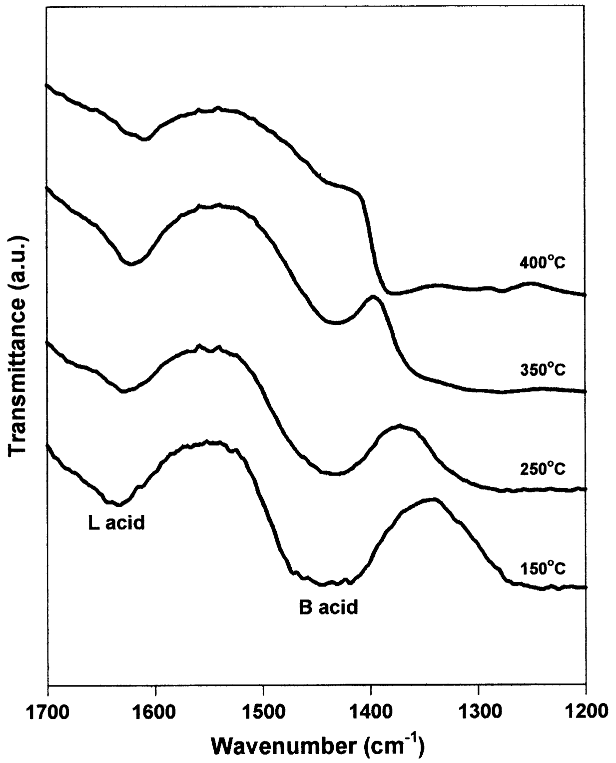

Fig. 6. IR spectra of ST500 catalyst adsorbing NH_3 with respect to evacuation temperature.

distinctive characteristic bands at 1,610 and 1,450 cm^{-1} corresponding to Lewis and Brønsted acid sites, respectively, as also observed in Fig. 5. The intensity of Lewis acid sites is hardly altered by the evacuation of the catalyst at temperatures up to 400 °C. However, the Brønsted acid site intensity has been gradually reduced within the range of the evacuation temperature. This may simply indicate that the Brønsted acid site is responsible for SCR reaction rather than the Lewis acid site. When the catalyst is evacuated at 400 °C, the Lewis acid site still exists on the catalyst surface based on IR spectra in Fig. 6. It should be noted that no characteristic band for $\nu(S=O)$ within the IR range from 1,300 to 1,400 cm^{-1} was observed at an evacuation temperature up to 350 °C probably due to the overlapping of the IR bands with NH_3. For the catalyst evacuated at 400 °C, the characteristic IR band for sulfur on the catalyst surface appears at 1,390 cm^{-1} mainly due to the desorption of NH_3 from the catalyst surface upon the increase of the evacuation temperature.

CONCLUSIONS

The NO removal activity of sulfated titania (ST) is strongly influenced by the surface acidity of the catalyst induced from the sulfur species on the catalyst surface. It has been observed that the presence of sulfur species on the catalyst surface is critical for the formation of acid sites. Although both Brønsted and Lewis acid sites on the surface of ST have been identified by IR study for the catalyst adsorbing NH_3 or pyridine as a probe molecule, the reduction of the intensity of IR band representing Brønsted acid sites is more pronounced than that of Lewis acid sites with respect to the calcination temperature of ST catalyst. The catalytic activity of NO removal for ST catalyst also decreases as the calcination temperature increases. The ST catalyst calcined at lower temperature contains larger amount of sulfur responsible for the generation of Brønsted acid sites on the surface of TiO_2. The simultaneous reduction of NO removal activity and Brønsted acid sites upon the increase of the calcination temperature indicates that Brønsted acid sites induced by sulfate are primarily important for enhancing the catalytic activity of NO reduction by NH_3 over ST catalyst.

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