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Poisoning Effect of SO_2 on NO Reduction by i-Butane over Fe/ZSM-5 Prepared by Sublimation Method

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X-ray photoelectron spectroscopy (XPS) ***in situ*** **electron paramagnetic resonance (EPR),** ***in situ*** **Fourier transform infrared spectroscopy (FT-IR), SO_2 temperature-programmed desorption (TPD), and reaction tests were performed to investigate the poisoning effect on the selective catalytic reaction of NO by i-butane over Fe/ZSM-5. Kinetic studies at 623 K, showed that the presence of SO_2 in the reaction mixture poisoned Fe/ZSM-5 irreversibly. XPS studies of Fe/ZSM-5 after reaction with SO_2 at 623 K revealed the formation of sulfate species, which corresponds well to the SO_2 TPD result.** ***In situ*** **EPR spectra showed that the lines arising from the distorted tetrahedral Fe^{3+} ions at $g \approx 5.8$ and 6.5, which were known to be reactive species, disappeared and a new and sharp one at $g \approx 1.9978$ assigned to paramagnetic coke species appeared. The preadsorption of SO_2 suppressed the formation of the IR bands arising from $Fe–NO_2$ ($1623\ cm^{-1}$) and $Fe–NO_3$ ($1573\ cm^{-1}$). On the basis of these results, SO_2 deactivated Fe/ZSM-5 by suppressing the formation of $Fe–NO_y$ ($y = 2, 3$) complexes and promoting the formation of carbonaceous deposits, which resulted in consumption of the active Fe^{3+} sites.** © 2001 Academic Press

Key Words: **selective catalytic reduction; Fe/ZSM-5; SO_2; electron paramagnetic resonance; infrared; X-ray photoelectron spectroscopy; temperature-programmed desorption; sublimation.**

INTRODUCTION

The selective catalytic reduction of NO in the presence of excess O_2 (SCR-NO) by hydrocarbons over several metal ion-exchanged zeolites has attracted much attention (1–3). Although Cu/ZSM-5 showed a high activity in SCR-NO, it had the drawbacks of reversible inhibition by H_2O and irreversible poisoning by SO_2 (4). Feng and Hall (5, 6) prepared over exchanged Fe/ZSM-5 by exchanging $[FeOH]^+$ ions into Na/ZSM-5 from oxalate solution. It was catalytically active and resistant to poisoning by H_2O and SO_2 for SCR-NO. Moreover, after a 25,000-h durability test, only a small loss of activity was observed. However, the authors mentioned that the results were not reproducible and were dependent largely on the history of the zeolite as well as the preparation conditions (7). Chen and Sachtler (8, 9) reported the active Fe/ZSM-5 made by sublimation of volatile $FeCl_3$, which had durability in the presence of H_2O. Contrary to the preparation method of Feng and Hall, the catalytic properties are not sensitive to the initial state of ZSM-5; an exchange level as high as $Fe/Al = 1$ can be easily obtained for the different types of H/ZSM-5 ($10 < Si/Al < 25$).

From a practical point of view, SCR-NO catalysts should be resistant to inhibition by SO_2 and H_2O in real exhaust gases which contain small amounts of sulfur compounds and H_2O. Although a promoting effect of H_2O on the SCR-NO over Fe/ZSM-5 prepared by the sublimation method was reported (9), the influence of SO_2 on the activity of Fe/ZSM-5 and the deactivation mechanism of SO_2 for SCR-NO has not been reported up to now. We report here that the activity of Fe/ZSM-5 prepared by the sublimation method decreased irreversibly in the SCR of NO by isobutane when SO_2 was present in the reaction mixture. The deactivation mechanism of Fe/ZSM-5 arising from SO_2 was investigated by using a combination of X-ray photoelectron spectroscopy (XPS), *in situ* electron paramagnetic resonance (EPR), *in situ* Fourier transform infrared spectroscopy (FT-IR), SO_2 temperature-programmed desorption (TPD), and reaction studies.

EXPERIMENTAL

Catalyst Preparation

The parent NH_4-ZSM-5 zeolite (ALSI-5, SM27, $Si/Al = 11.75$) was transformed into H/ZSM-5 by calcination in O_2 flow at 773 K for 4 h. Fe/ZSM-5 was prepared by the sublimation method as described by Sachtler and co-workers (8, 9). The sample was washed with deionized H_2O. After drying, it was calcined for 2 h in flowing O_2 at 873 K for 4 h. ICP-AES results indicated that the molar ratio of Fe to Al was 1.06.

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Reaction Studies

The catalytic tests were carried out in a continuous-flow quartz reactor. Before experiments, the catalyst was calcined in O_2 at 873 K for 2 h. A reaction gas mixture of 0.2% NO, 3% O_2, 0.2% i-butane, and, when desired, 150 or 300 ppm SO_2 was fed to 0.1 g of catalyst at a rate of 140 cm^3/min (with He balance and GHSV = 42,000 h^{-1}). The products were analyzed with GC (HP 5840A, Propak Q: i-butane and CO_2; molecular sieve 5A: N_2 and CO) and NO_x analyzer (ThermoEnvironmental 42H).

EPR Measurements

EPR spectra at 9.2 GHz (X band) were recorded at RT and 77 K with a Bruker ESP-300 EPR spectrometer. α,α-Diphenyl-β-picrylhydrazyl (DPPH) was used to calibrate the g values (spectroscopic splitting factors). An *in situ* EPR quartz reactor with a side-arm tube designed to avoid air contact was used as the EPR cell (10). The EPR spectra were taken at a microwave power of 2.4 mW and modulation amplitude of 3.8 G in the field range 200–4800 G. All spectra were recorded with a scale of 20.

XPS Measurements

XPS spectra were acquired with a surface analysis system (LHS-10, SPECS GmbH) equipped with a multichannel detector using MgKα radiation (300 W). The pass energy was 71 eV. Pelletized Fe/ZSM-5 was treated with SO_2 at 573 K for 30 min in the high-pressure reaction cell and transferred directly to the main chamber without exposure to air. Binding energies were referenced to Si 2p at 102.9 eV from ZSM-5 zeolite.

TPD (Temperature Programmed Desorption) of SO_2

Before the TPD experiments, Fe/ZSM-5 was calcined in a quartz microreactor at 873 K in an O_2 flow of 50 cm^3/min for 2 h. After cooling down in a He flow, He was changed to the gas mixture 10 vol% SO_2/He with a flow of 10 cm^3/min and connected to the chemiluminescent SO_2 analyzer (43°C, ThermoEnvironment). Following saturation of the sample with SO_2, Fe/ZSM-5 was purged in He flow to remove all reversibly adsorbed SO_2 until the effluent SO_2 was stabilized. TPD of SO_2 was carried out in a He flow of 50 cm^3/min up to 1073 K at a heating rate of 4 K/min.

In Situ FT-IR Measurements

FT-IR spectra were acquired using an *in situ* cell installed in a Nicolet Magna 560 FT-IR spectrometer with an MCT detector. The cell was equipped with KBr windows. After calcination at 873 K in an O_2 flow of 50 cm^3/min, the Fe/ZSM-5 sample was pressed into a self-supporting disk of 10–25 mg/cm^2. The self-supporting disk was pretreated under vacuum at 623 K for 2 h. It was then cooled down to 473 K in He flow. Experiments were carried out at 473, 523, 573, and 623 K. For NO + O_2 adsorption, a gas mixture of NO (0.4%) + O_2(3%) + He at a total flow of 70 cm^3/min was used. Both adsorption and desorption were carried out for 0.5 h. Desorption was carried out in a He flow of 45 cm^3/min. For SO_2 adsorption a gas mixture of SO_2 (0.2%) + He at total flow of 70 cm^3/min was used. All spectra were recorded by accumulating 1000 scans with a spectral resolution of 4 cm^{-1}. The IR spectra reported in this paper were subtracted from the spectrum of the calcined sample measured under He flow conditions.

RESULTS AND DISCUSSION

Effect of SO_2 on the Catalytic Activity

The catalytic activity of SCR-NO by i-butane over Fe/ZSM-5 results in maximum conversion of NO at 623 K, which is in good agreement with previous results (8, 9). Table 1 indicates the effect of SO_2 in the reaction mixture on SCR-NO at 623 K, the temperature at which the maximum conversion of NO was obtained. Our kinetic results of SCR-NO with i-butane show that the conversion of NO to N_2 decreases from 59.1 to 36.0% when 150 ppm SO_2 is present in the reaction mixture. When SO_2 is removed from the reaction mixture, the conversion increases to 43.8%, indicating irreversible inhibition by SO_2. Moreover, when a larger amount of SO_2 is added to the reaction mixture, the degree of deactivation becomes higher; 300 ppm of SO_2 deactivates the Fe/ZSM-5 more drastically to 24.7% NO conversion. Previous works reported that SO_2 led to the poisoning of reaction sites by the formation of sulfates or sulfides species. Okazaki *et al.* (12) investigated the deactivation in the NO-SCR over Fe/Al_2O_3 with SO_2, which is attributed to the formation of $FeSO_4$-like species. Along with a decrease in the conversion of NO, it is observed that a decrease in hydrocarbon oxidation to CO and CO_2 also occurs in the presence of SO_2. In summary, SO_2 in the reaction mixture irreversibly poisons N_2 reduction as well as hydrocarbon oxidation over Fe/ZSM-5.

TABLE 1

Catalytic Activity of Fe/ZSM-5 in NO-SCR in the Presence of SO_2 at 623 K

	No conversion to N_2 (%)	i-Butane conversion to CO (%)	i-Butane conversion to CO_2 (%)
Before SO_2 treatment	59.1	40.0	31.9
After treatment of 150 ppm SO_2	36.0	21.5	13.6
In the absence of SO_2	43.8	27.0	20.6
After treatment of 300 ppm SO_2	24.7	15.0	9.1
In the absence of SO_2	36.5	20.6	17.0

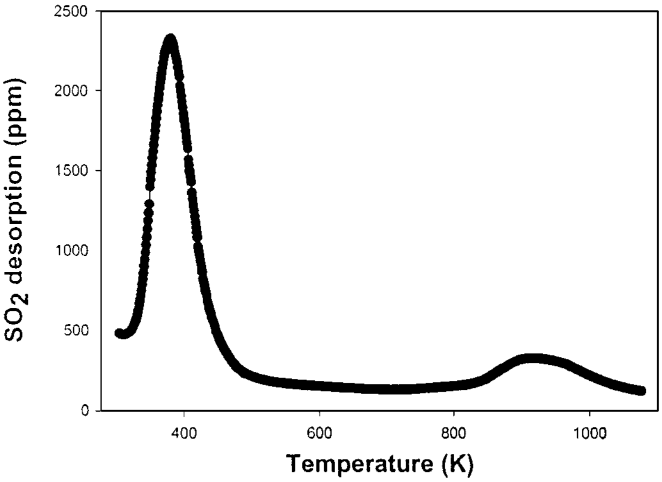

FIG. 1. Temperature-programmed desorption of SO_2 over Fe/ZSM-5.

Adsorption Behavior of SO_2 on Fe/ZSM-5

To study the adsorption behavior of SO_2 on Fe/ZSM-5, TPD and XPS experiments were carried out. As shown in Fig. 1, two peaks in SO_2 TPD are observed: one at about 393 K and a weaker but very broad peak at 900 K. The first peak can be assigned to physically adsorbed SO_2. The broad peak at 900 K may be attributed to the decomposition of surface sulfate- or/and sulfite-type surface species, resulting from the adsorption of SO_2 on basic O_2^- sites (11). The S $2p$ photoelectron spectrum of Fe/ZSM-5 pretreated with SO_2 at 623 K reveals the presence of sulfate-like species as shown in Fig. 2. The S $2p_{3/2}$ binding energy of 169.4 eV is very close to the 169.2 eV assigned to $FeSO_4$ (12). No XPS peaks between 161.0 and 162.8 eV for sulfides and at 164 eV for elemental sulfur were observed. Both TPD and XPS studies clearly demonstrate that SO_2 exists as a form of sulfate on Fe/ZSM-5 at 623 K.

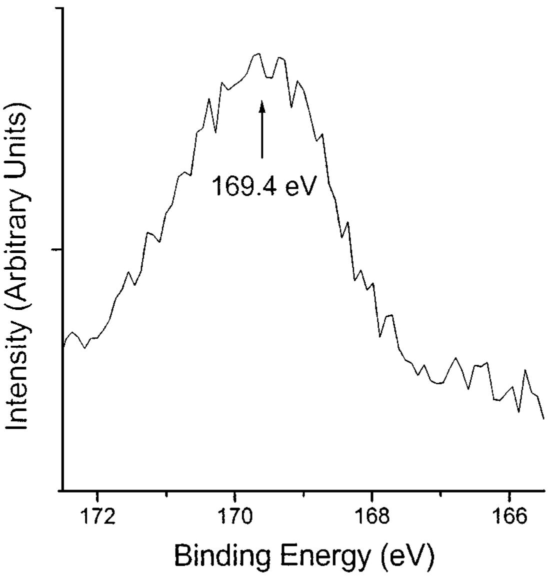

FIG. 2. S $2p$ photoelectron spectrum of Fe/ZSM-5 pretreated with SO_2 at 623 K.

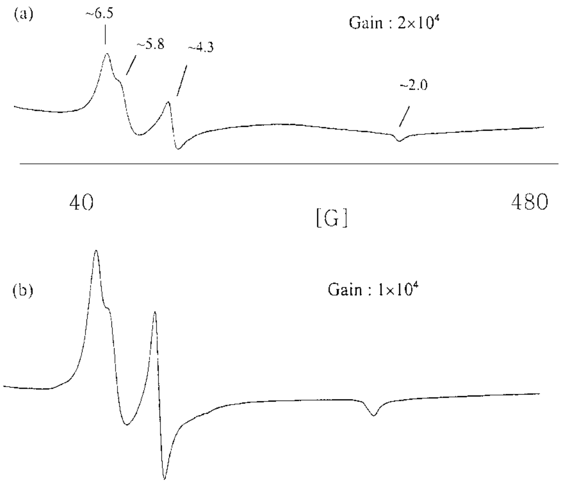

FIG. 3. EPR spectra of Fe/ZSM-5 after calcination recorded at RT (a) and 77 K (b).

In Situ EPR Studies

Fe^{3+} ions in the zeolite system occupy the $^6S_{5/2}$ ground electronic Russel–Saunders state for high-spin d^5 ions. Therefore, EPR spectroscopy is very useful in investigating zeolites containing Fe^{3+} since the EPR parameters of Fe^{3+} depend on the local crystal field. Calcination of Fe/ZSM-5 in O_2 at 873 K results in the EPR lines at $g \approx 6.5$, $g \approx 5.8$, and $g \approx 4.28$ as depicted in Fig 3. According to previous work, the lines at $g \approx 6.5$ and $g \approx 5.8$ are assigned to distorted tetrahedral Fe^{3+} and that at $g \approx 4.28$ to tetrahedral Fe^{3+} (13–15). We also observe the weak line at $g \approx 2.0$ arising from Fe^{3+} with octahedral symmetry in a cationic position (13). In addition, there is no EPR line at $g \approx 2.3$, which is characteristic of the Fe^{3+} ion in the iron oxide (Fe_2O_3) phase. This result indicates that the majority of the Fe^{3+} ions in Fe/ZSM-5 are isolated in distorted or less distorted tetrahedral coordination.

After NO-SCR at 623 K as shown in Fig 4b, the signals arising from distorted tetrahedral coordination decreased

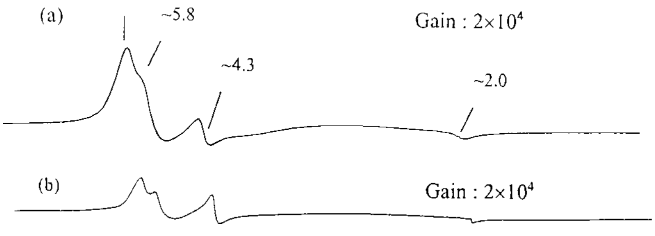

FIG. 4. EPR spectra of Fe/ZSM-5 after calcination (a) and after SCR reaction of NO at 623 K (b) recorded at RT.

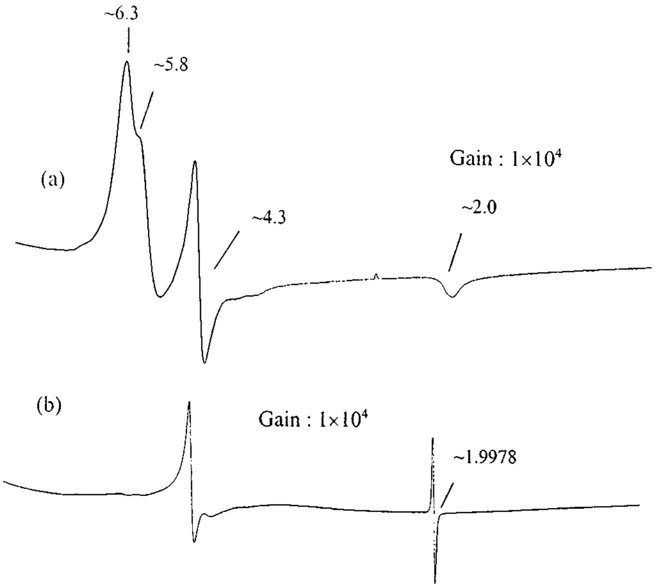

FIG. 5. EPR spectra of Fe/ZSM-5 after calcination (a) and after SCR reaction of NO at 623 K when SO_2 was present (b) recorded at 77 K.

in the EPR spectra. On the contrary, a line at $g \approx 4.28$ changed insignificantly. In other words, the former species take part in the catalytic cycle while the latter does not. Lee and Rhee (16) reported that the concentration of isolated Fe^{3+} cations in distorted tetrahedral coordination was correlated with the reactivity of the catalysts. In the same manner, the active centers seem to be mainly distorted tetrahedral Fe^{3+} species at $g \approx 5.8$ and $g \approx 6.5$.

When SO_2 is present in the reaction mixture, the lines at $g \approx 5.8$ and $g \approx 6.5$ disappear completely and the line at $g \approx 4.28$ decreases a little as shown in Fig. 5b. This provides the evidence that Fe^{3+} with distorted tetrahedral coordination are poisoned by SO_2. It implies that SO_2 plays a crucial role in reducing the active sites, which are distorted tetrahedral Fe^{3+}.

A signal at $g \approx 1.9978$ which was observed after SCR reaction of NO in the presence of SO_2 can be assigned to hexacoordinated Fe^{3+} complex with octahedral symmetry. However, the formation of Fe^{3+} species is not probable because Kucherov *et al.* (17) observed the reduction of Fe^{3+} to Fe^{2+} after treating Fe/ZSM-5 with C_3H_6 at 523 K. Hence, we can exclude the possibility of assigning the peak to hexacoordinated Fe^{3+} complex with octahedral symmetry.

The next candidate for the assignment of this signal at $g \approx 1.9978$ is the paramagnetic coke species because the color of Fe/ZSM-5 was changed from red-yellow to dark brown. Moreover, the conversion of isobutane to CO and CO_2 decreased from 71.9 to 35.1% in the presence of 150 ppm SO_2 and to 24.1% in the presence of 300 ppm SO_2. This peak at $g \approx 1.9978$ was recorded after the adsorption of i-butane followed by heating *in vacu* at 523 and 623 K as shown in Fig. 6, and the color of the catalyst changed to dark brown, too. Kucherov and Slinkin (15) reported that calcination of solid-state ion-exchanged Fe/ZSM-5 with *p*-xylene sorbed at 293 K led to the formation of coke, producing a narrow EPR line with $g \approx 2.002$ typical of *p*-xylene cation radicals. Therefore, it is concluded that SO_2 facilitates coke formation on the surface during NO-SCR in the presence of SO_2.

In Situ FT-IR Studies

The FT-IR spectrum observed after the adsorption of NO and O_2 at 473 K is shown in Fig. 7a. Sachtler *et al.* assigned the bands around 1624 cm^{-1} to a nitro group ligated to an iron ion and those at 1573 cm^{-1} to a nitrate group on an iron site (18). The band at 1884 cm^{-1} has been assigned to

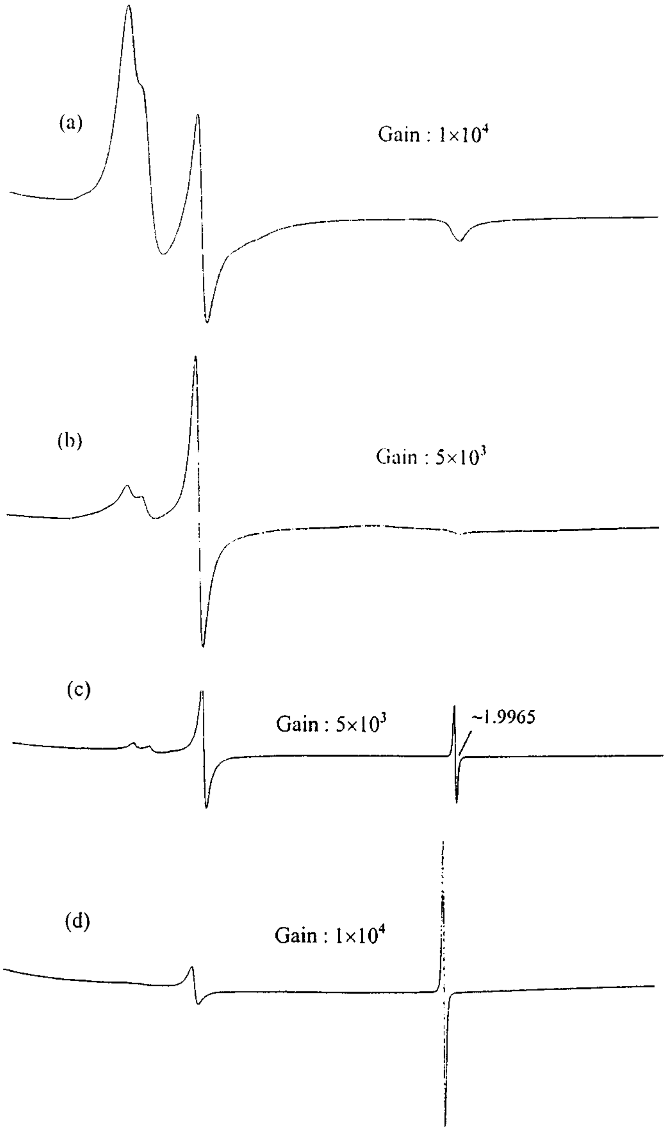

FIG. 6. EPR spectra of Fe/ZSM-5 after calcination (a) and adsorption of i-butane (b) and followed by heating *in vacu* at 523 K (c) and 623 K (d) recorded at 77 K.

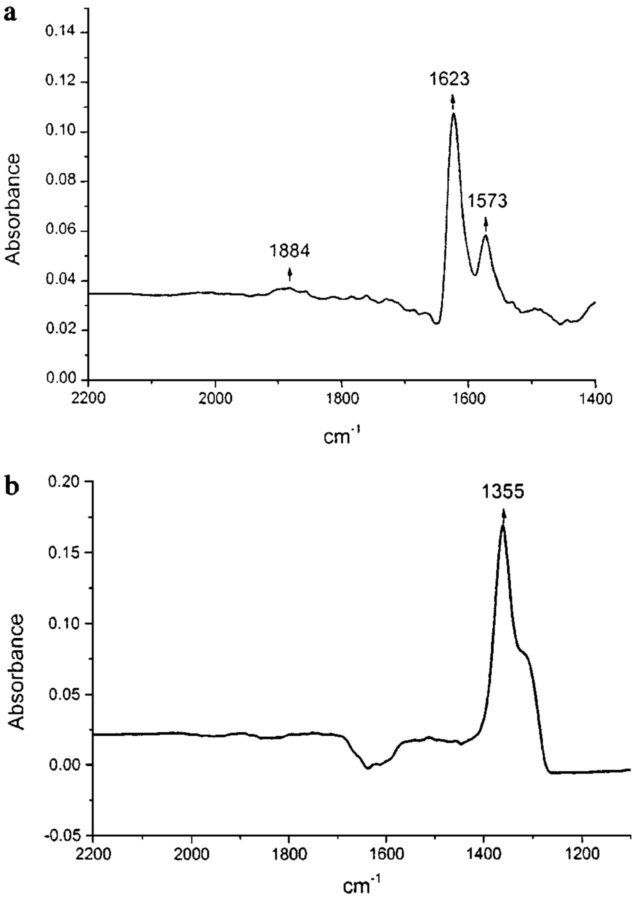

FIG. 7. FT-IR spectra NO and O_2 adsorbed on Fe/ZSM-5 at 473 K followed by He purging. (a) Fe/ZSM-5 was calcined at 873K; (b) 0.2% of SO_2 was preadsorbed after calcinations at 873 K.

the iron mononitrosyl complex formed by the interaction of NO with iron (18–20). FT-IR spectra of NO and O_2 at 473 K show the formation of nitro/nitrate species similar to those of Sachtler and co-workers (18). He suggested that the formation of nitro/nitrate on the Fe/ZSM-5 is the first step in the reaction mechanism. However, after preadsorption of SO_2 followed by adsorption from a mixture of NO and O_2, bands around 1623 and 1573 cm^{-1} disappear completely, as shown in Fig. 7b. It shows only a strong band around 1358 cm^{-1} and a shoulder at 1322 cm^{-1}. The S=O stretching vibration of metal sulfates usually lies around 1235–1100 cm^{-1} (21). The band around 1370 cm^{-1} was assigned to the asymmetric vibration of S=O bands of the sulfate which is in agreement with the results on Fe_2O_3 (22). The band at 1355 cm^{-1} can be assigned to the asymmetric vibration of S=O bands of the sulfate complexed on Fe^{3+} of Fe/ZSM-5. It is a significant result that SO_2 inhibits the formation of nitro/nitrate species on Fe/ZSM-5.

Role of SO_2 in SCR-NO over Fe/ZSM-5

This study shows that the conversion of NO to N_2 with i-butane at 623 K, catalyzed over Fe/ZSM-5 prepared by sublimation, decreases from 59 to 36% when 150 ppm of SO_2 is present in the reaction mixture. The catalyst does not recover its original activity even after SO_2 is removed. This is irreversible poisoning. It was shown that SO_2 exists as a form of sulfate on the surface. Based on the characterization results, the role of SO_2 in NO-SCR over Fe/ZSM-5 is summarized as follows.

First, SO_2 inhibits the formation of nitro/nitrate species by forming sulfate on the surface. Sachtler and co-workers (18) suggested that the first step of the SCR reaction is formation of chemisorbed complexes of NO_y with $y \geq 2$, and a nitrogen-containing deposit (nitrile, isocyanate or amine) impedes the reaction of NO and O_2. Also, Bell and co-workers (23) proposed a mechanism for reduction of NO by C_3H_8 over Fe/ZSM-5, which includes NO_2 formation as the first step. Our IR study clearly demonstrated that preadsorption of SO_2 prevented the Fe/ZSM-5 from forming the NO_2/NO_3 species on the surface. In other words, SO_2 appears to occupy the active sites preferentially in the form of sulfate species as evidenced from our TPD, XPS, and IR results.

The second role of SO_2 is to lower the rate of hydrocarbon oxidation, which results in the production of coke on the Fe/ZSM-5. In the absence of SO_2, N-containing deposits, which are suggested to be nitrile, isocyanate, or amine species, react with different adsorbed NO_2 or gas-phase NO_2 molecules to form N_2 (21). SO_2 seems to inhibit this reaction, resulting in the formation of N-containing deposits; it promotes coke formation. SO_2 plays a role in delaying the complete oxidation of i-butane to CO_2. Instead, it accelerates the coke formation.

Third, the reactive distorted tetrahedral Fe^{3+} species disappears in the presence of SO_2. As suggested in previous studies (16, 17), the distorted tetrahedral Fe^{3+} species plays an important role as an active site for NO-SCR over Fe/ZSM-5. Therefore, the disappearance of this species is one of the reasons for the deactivation. What kinds of molecules interact with this Fe^{3+} species is an open question. SO_2 does not interact considerably with the Fe^{3+} species from the fact that the lines at $g \approx 5.8$ and $g \approx 6.5$ still exist after the treatment with SO_2 at 523 K (not shown). As the temperature increases after preadsorption of i-butane, the consumption of these peaks is revealed in Fig. 6. Hence i-butane is likely to strongly interact with the distorted tetrahedral Fe^{3+} sites in the middle of the coking process. If SO_2 is absent from the reaction mixture, i-butane seems to be involved in the catalytic cycle by making the N-containing deposits as suggested by Sachtler (20), without consumption of the active Fe^{3+} species. However, SO_2 plays an important role in preventing i-butane from taking part in the mechanism and, consequently, letting i-butane block the active Fe^{3+} sites as a form of coke.

In summary, SO_2 deactivates Fe/ZSM-5 by suppressing formation of the Fe–NO_2 complex and increasing formation of carbonaceous deposits, thus resulting in the disappearance of the reactive distorted tetrahedral Fe^{3+} sites.

CONCLUSIONS

This article describes the poisoning effect of SO_2 on SCR-NO by i-butane over Fe/ZSM-5 prepared by sublimation using XPS, *in situ* EPR, *in situ* FT-IR, and SO_2 TPD, which is correlated to catalytic activity. It was shown from the reaction data at 623 K that addition of SO_2 to the reaction mixture poisoned Fe/ZSM-5 irreversibly. XPS and TPD clearly demonstrated that SO_2 existed as a form of sulfate species. *In situ* EPR data showed that the signals arising from the distorted tetrahedral Fe^{3+} ions at $g \approx 5.8$ and $g \approx 6.5$, which are known to be highly reactive species, disappeared. Instead, a new and sharp signal at $g \approx 1.9978$ assigned to paramagnetic coke species appeared. The preadsorption of SO_2 suppressed formation of the IR bands arising from $Fe–NO_2$ ($1623\ cm^{-1}$) and $Fe–NO_3$ ($1573\ cm^{-1}$). On the basis of these results, SO_2 deactivated Fe/ZSM-5 by suppressing the formation of $Fe–NO_y$ ($y = 2, 3$) complexes and increasing the formation of carbonaceous deposits, which preferentially deactivated the active distorted tetrahedral Fe^{3+} sites.

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