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An infrared study of the behavior of SO_2 and NO_x over carbon and carbon-supported catalysts

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Abstract

The heterogeneous reactivity of NO_x and SO_2 with carbon has been investigated with FT-IR spectroscopy. The interaction between NO and SO_2 on carbon surface have been studied in the presence and in the absence of oxygen. Thermal stabilities of surface structures, formed as a result of NO_x and SO_2 chemisorption have been determined by means of FT-IR spectroscopy. During the reaction of NO/O_2 mixture with carbon the surface species, including C–NO_2, C–ONO, C–NCO and anhydride structures are formed. It has been found that SO_2 retards the oxidation reaction of carbon by oxygen. The oxidation of SO_2 on carbon was found to be greatly enhanced by the presence of NO + O_2 mixture. The adsorption capacity of cellulose based carbon, catalytic NO_x decomposition and TPD was studied using a fixed bed flow reactor.

Keywords: SO_2; NO_x; Carbon-supported catalyst

1. Introduction

Processes for the reduction of SO_2 and NO_x pollution are among the most investigated in the field of environmental catalysis today [1,2]. The simultaneous occurrence of the reduction of SO_2 and NO_x is an important research topic in heterogeneous catalysts. Active carbon has been recognized as one effective adsorbent and catalyst in processes of adsorptive-catalytic cleaning of stack gases [3–7]. The reduction of NO_2 to N_2 without the use of an externally supplied reductant can be achieved with carbon [8]. We found that carbon-supported Pt catalyst had a very high activity for the decomposition of NO in the absence of oxygen [9].

Although much effort has been given to elucidate the mechanism of SO_2 and NO oxidation there is a considerable lack of information on the surface species formed as a result of interaction of SO_2 and NO_x with carbon. It was shown in Ref. [3] that NO_x enhances SO_2 adsorption.

In the literature, different mechanisms have been proposed for de-SO_2 and de-NO_x on the surface of carbon but the true pathways still being unambiguously recognized.

It seems that carbon and carbon-supported catalysts activity is strongly influenced by intermediates formed as a result of the interaction between the surface of carbon and SO_2 or nitrogen oxides.

IR spectroscopy provides information on the nature of bonds formed between adsorbates and the surface of catalysts; it provides a unique means to obtain information on the intermediates and products formed on the surface of carbons. IR spectroscopy of carbon and carbon-supported catalysts has not received much attention due to the difficulty in obtaining IR spectra of these highly opaque samples. Due to the application of carbon film technique the problems of experimental spectroscopic investigations of surface phenomena on carbon have been solved to a great extend [8–11]. Because SO_2 and NO_x may undergo several different reactions on surfaces to yield surface-bound and gas-phase products, it is important in any laboratory study of heterogeneous reactions that both gas phase and surface-bound species are probed. A complete characterization of all reaction products and intermediates makes it possible for the details of the reaction mechanism to be discerned.

The purpose of this work is to study the adsorption of SO_2 and NO and their co-adsorption with a view of identifying intermediate species. It should be noted, however, that the surface complexes formed can be fairly stable and may not necessarily be reaction intermediates.

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2. Experimental

Carbon films used in this study were prepared from cellulose carbonized at 600 °C Infrared spectroscopic studies were carried out in a vacuum cell described previously [11]. For the *in situ* IR study of the heterogeneous reactions a carbon film samples were exposed to SO_2, SO_2/O_2, NO, NO/O_2, NO/SO_2 and $NO/SO_2/O_2$ mixture. In the present paper, the adsorption and oxidation of SO_2 and NO over cellulose based carbon were investigated without the presence of water. The composition of the gas phase in contact with the catalyst was also monitored by FT-IR. The ratio of the single beam spectrum with gases in the beam to that with the carbon and gases allows the gases absorption to be rationed out, giving the absorbance due to carbon with adsorbed species.

Measurements of catalytic activity for the gas mixture conversion and kinetic studies were performed in a flow microcatalytic reactor, under atmospheric pressure. The reactor was a 4 mm i.d. quartz tube. The gases were fed from compressed cylinders. Flow rates of the feed gases were adjusted with Tylan mass flow controller. The gases were analyzed before and after passing over the catalyst with FT-IR (Mattson-Genesis II) using multiple-pass gas cell (Sirocco cell with the path length of 2 m), which was attached to the flow system [8].

Before introducing the reactant mixture the samples were pretreated in the reactor under an Ar flow at 400 °C for at least 1 h, and then cooled to the desired temperature. The reaction mixture was kept flowing for 3 h until steady-state conditions were attained.

3. Results and discussion

Although it is generally understood that oxygen enhances the NO adsorption and reduction by carbon [8,12,13] the forms of adsorbed species and effect of oxygen need to be further investigated. Infrared spectroscopy has proven to be a valuable tool in studies of the carbon–NO_x reactions under varying conditions of temperature, pressure and concentrations of the reactant species. FT-IR spectra of carbon sample after exposure to NO/O_2 mixture at increasing temperatures are displayed in Fig. 1. Carbon film outgassed at 600 °C (spectrum 1) shows the presence of an absorption band at 1600 cm^{-1} and mutually overlapping bands in the region of 1100–1500 cm^{-1}. The spectral features of carbon film obtained at 600 °C in vacuum were described earlier [10].

Fig. 1 shows that after adsorption of NO without the presence of oxygen (spectrum 2) the intensities of all the IR features change very little, suggesting that very small amount of NO is adsorbed and reacts with the surface of carbon under conditions of this study.

When such a sample was exposed to NO/O_2 mixture, some new bands attributed to adsorbed NO_x species appeared in the spectrum. The occurrence of different surface species that are dependent on adsorption temperature yields important clue about the chemistry of NO/O_2 reaction on carbon. The chemisorption of oxygen at room temperature (spectrum 3) leads to intensity increase of the 1600 cm^{-1} band and the bands in the range of 1100–1500 cm^{-1}. Thus, the IR spectroscopic studies showed the formation of ion-radical surface compounds in the initial phase of oxygen chemisorption [11]. The formation of surface oxygen species (spectrum 4) leads to a progressive increase of the bands at 1747 and 1713 cm^{-1} as well as of the bands in the range of 1200–1400 cm^{-1}.

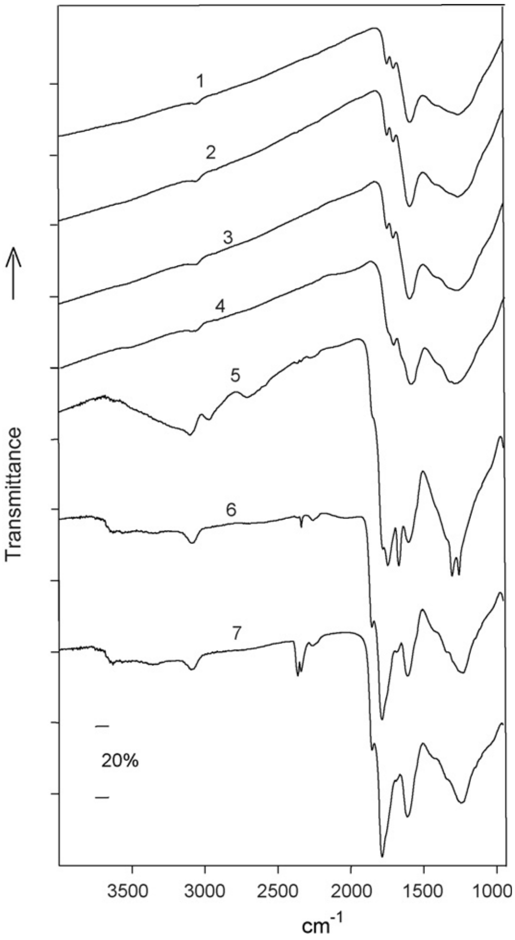

Fig. 1. FT-IR spectra of carbon film exposed to NO + O_2 mixture: (1) carbon film after outgassing at 600 °C, (2) after contact with NO at 12.1 Tr at 25 °C, (3) after contact with NO (12.1 Tr) + O_2 (760 Tr) at 25 °C, (4) 100 °C, (5) 200 °C, (6) 250 °C, and (7) 300 °C.

After exposure of carbon film to the mixture of NO/O_2 at 200 °C (spectrum 5) more distinct absorption bands become apparent with frequencies of 1851, 1782 and 1743 cm^{-1}. The results suggest that two bands at 1851 and 1782 cm^{-1} are due to newly formed carbon oxygen functionalities, probably lactone and anhydride groups. The band at 1743 cm^{-1} can be attributed to the C=O stretching frequency of carboxylic structures. There are several other absorption bands present in the spectrum with frequencies of 1667, 1302 and 1254 cm^{-1}. The bands at 1302 and 1254 cm^{-1} are assigned to the ν_1 and ν_3 modes, respectively, of chelating bridging nitrito species. It has been shown that NO and NO_2 can react with carbon to produce HONO [14]:

$$NO + OH \rightarrow HONO \quad (1)$$

$$NO + NO_2 + H_2O \rightarrow 2HONO \quad (2)$$

As shown in Fig. 1 the bands at 1743 and 1254 cm^{-1} may also be assigned to the ν(N=O) and δ(HON) modes respectively of adsorbed HONO. Simultaneously a new IR feature grows in O–H stretching region. The shape of the band of O–H stretching vibrations indicates (spectrum 5) that O–H groups are linked by hydrogen bonds. The band at 2969 cm^{-1} may be identified as $\nu_1 + \nu_3$ band of NO_2.

Heating the sample leads to a significant decrease of the band at 1667 cm^{-1}. After heat treatment at 250 °C, the bands at 1302 and 1254 cm^{-1} completely disappeared (spectrum 6).

The reaction of carbon with NO/O_2 mixture at 300 °C leads to the progressive increase of the bands at 1851 and 1782 cm^{-1} (spectrum 7). It should be pointed out that $NO + O_2$ reaction with carbon at 250–300 °C leads to the formation of 2256 cm^{-1} band of isocyanate species. NCO species may originate from the reaction between NO and CO. Carbon monoxide is formed as a result of chemisorption of oxygen on the surface of carbon as well as the small thermal decomposition of oxygen containing surface functional groups. However, it is not clear whether these isocyanate species are intermediates in NO_x decomposition, or they are simply undesired side products hampering the efficiency of the decomposition process.

In our previous study [9] a carbon obtained from cellulose showed a very low activity toward NO decomposition. Results, reported in Ref. [8] show that in the presence of oxygen the catalytic activity of carbons towards NO conversion to N_2 is much higher than in the absence of oxygen.

The results of IR spectroscopic investigations concerning the thermal stability of surface functional groups formed as a result of NO/O_2 interactions are shown in Fig. 2 (spectras 1–7).

No substantial changes in the intensity of the 1851 and 1782 cm^{-1} bands have been observed after evacuation up to 450 °C. IR spectroscopic studies of thermal stability of surface compounds reveal fact that during the outgassing at 450 °C their destruction occurs to only a small degree (spectrum 5). Outgassing at 500 °C brings only minor destruction of oxygen surface compounds. It is interesting to note that not substantial changes (spectrum 6) in the intensity of the NCO band have been observed after evacuation at 500 °C, i.e. the NCO species are stable at this temperature. Heating the carbon sample to 600 °C resulted in the decomposition of NCO surface species. It should be noted that the band at 2256 cm^{-1} is not present in the spectrum 7. The absorption bands at 1851 and 1779 cm^{-1} disappear almost completely after outgassing at this temperature. The carbon film outgassed at 600 °C reveals the absorption at 1590 cm^{-1} and the absorption of overlapping bands within 1500–1000 cm^{-1} range.

Recently, we observed that after adsorption of NO_2 on carbon film [8] FT-IR spectra are basically similar to those for NO/O_2 mixture adsorbed on the surface of carbon (Fig. 1). These experiments demonstrated that the NO_2 reactant was the origin of the oxygen atoms of all new functionalities.

It was shown in previous publication [10] that the simultaneous adsorption of SO_2 and O_2 occurs with the participation of π electrons of condensed aromatic system of carbon.

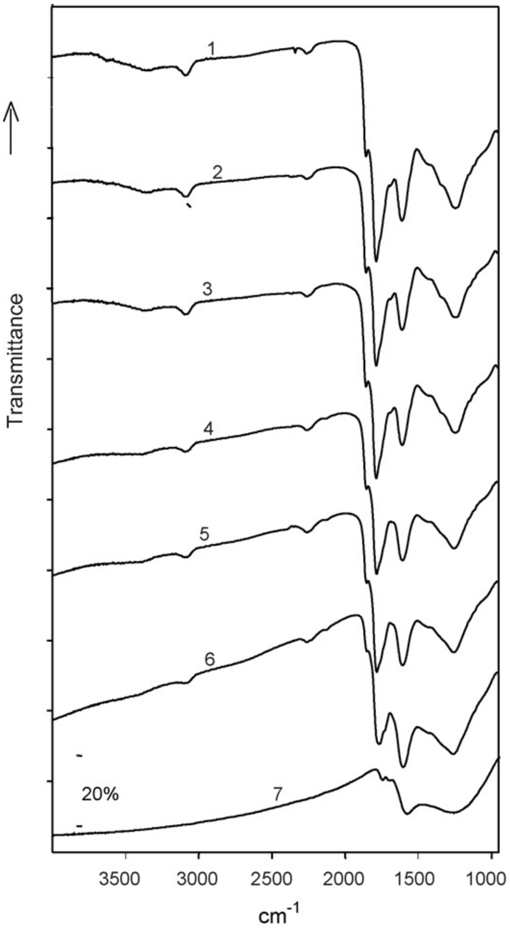

Fig. 2. FT-IR spectra of carbon film exposed to $NO + O_2$ mixture after outgassing at increasing temperatures: (1) after 30 min evacuation at 25 °C, (2) 200 °C, (3) 300 °C, (4) 400 °C, (5) 450 °C, (6) 500 °C, and (7) 600 °C.

The effects of, and roles played, by the surface oxygen functionalities on the catalytic oxidation of SO_2 have been studied extensively. The mechanism of oxidation of SO_2 on the surface of carbon is a most challenging problem.

The results of spectroscopic studies on the interaction of SO_2 with carbon are presented in Fig. 3. FT-IR spectra of carbon recorded after adsorption of SO_2 at room temperature without the presence of oxygen do not show any changes caused by the chemisorption of carbon–sulfur surface complexes. The bands at 1330 and 1140 cm^{-1} could be assigned to ν_3 and ν_1 vibrations of physically adsorbed SO_2, respectively. The oxidation of carbon film at 300 °C (Fig. 3, spectrum 6) leads to the formation of bands at 1744 and 1715 cm^{-1} in the range of C=O stretching vibrations. The bands at 1330 and 1140 cm^{-1} as well as small band at 1045 cm^{-1} present in the spectrum 6 indicate that there were at least two forms of SO_2 species on the surface of carbon. The definite identification of this species responsible for the 1045 cm^{-1} band is difficult. The appearance of this band suggests that the sulfite or SO_3 species are formed on the surface of carbon. Thus, the adsorption of SO_2 decreased the number of sites suitable for chemisorption of oxygen. It is clear that the retardation of the oxidation rate of carbon by O_2 is due to adsorbed SO_2.

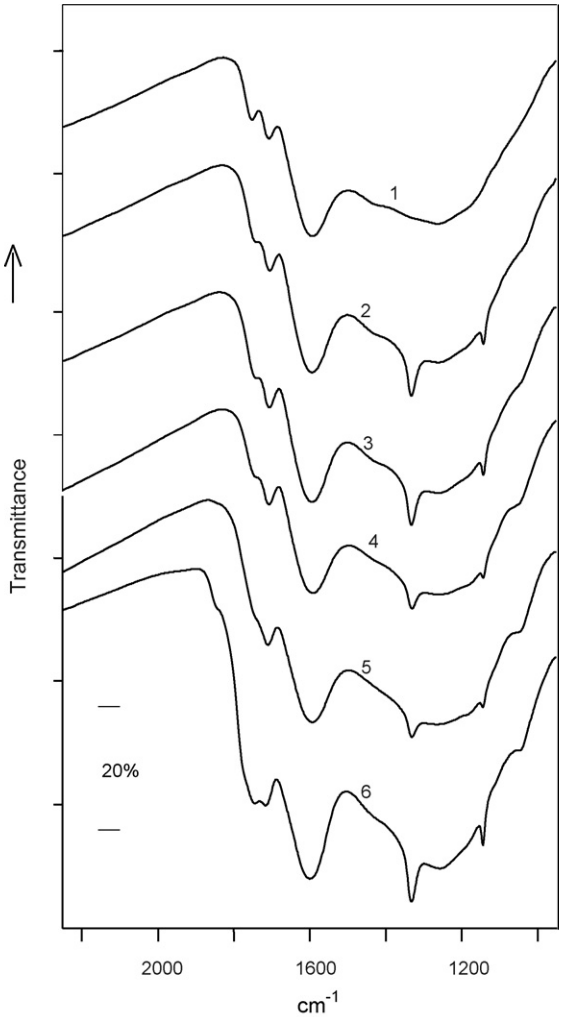

Fig. 3. FT-IR spectra recorded after exposure of carbon film to SO_2: (1) carbon film after outgassing at 600 °C, (2) after 30 min contact with SO_2 (12.3 Tr) at 25 °C, (3) after contact with SO_2 at 300 °C, (4) after contact with SO_2 (12.3 Tr) + O_2 (760 Tr) mixture at 25 °C, (5) 200 °C, and (6) 300 °C.

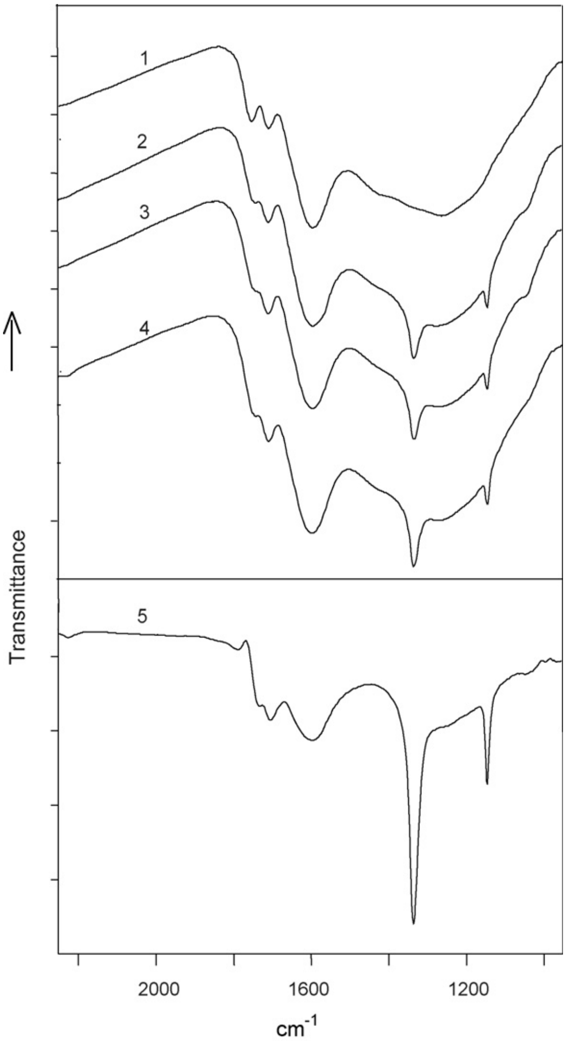

Fig. 4. FT-IR spectra of carbon film exposed to NO + SO_2 mixture: (1) carbon film after outgassing at 600 °C, (2) after 30 min contact with NO (6.7 Tr) + SO_2 (13.5 Tr) mixture at 25 °C, (3) 200 °C, (4) 400 °C, and (5) IR spectrum 4 from which the spectrum 1 has been subtracted.

FT-IR spectra of carbon sample after exposure to NO/SO_2 mixture at increasing temperature are displayed in Fig. 4. The carbon film outgassed at 600 °C (spectrum 1) does not contain any acidic carbon surface oxides. The adsorption of NO + SO_2 mixture on carbon film (spectras 2–4) causes the formation of physically adsorbed bands at 1330 and 1140 cm^{-1} while the band of adsorbed NO is not detected. It is interesting to note that exposure of NO + SO_2 to the carbon at higher temperature gave rise to the small bands at 1701 and 1729 cm^{-1}, which indicate that some of oxygen containing surface group are formed. The evidence for the formation of a week bands at 1600–1800 cm^{-1} region (spectrum 5) was obtained by subtracting spectrum 1 from spectrum 4 (Fig. 4). Oxygen, originating from NO/SO_2 decomposition reaction, can react with carbon surface to produce these small bands.

Fig. 5 shows the infrared spectra obtained after exposing the carbon sample to NO + SO_2 + O_2 mixture at increasing temperatures. Co-adsorption of NO + SO_2 in the presence of oxygen at 25 °C is accompanied by formation of oxygen-containing surface group at 1717 cm^{-1}. After the exposure of carbon to the mixture of NO/SO_2/O_2 at room temperature more distinct absorption band become apparent with frequency of 1052 cm^{-1} originated from chemisorbed SO_2. The bands at 1328 and 1144 cm^{-1} (spectras 2–8) being solely to SO_2 adsorbed physically, were much weaker than they had been after admission SO_2/NO (Fig. 4) or SO_2/O_2 mixture (Fig. 3). Pre-adsorption of NO/O_2 mixture on carbon surface resulted in considerable blocking the number of active sites for physical adsorption of SO_2.

In this study, the IR technique was applied to detect the difference in the interaction of carbon with NO/O_2 mixture and with NO/SO_2/O_2 mixture.

After reaction of NO/SO_2/O_2 mixture with carbon surface at 100–150 °C (spectras 3 and 4) the 1717 cm^{-1} peak intensifies and shifts to 1726 cm^{-1}. Co-adsorption of NO/SO_2/O_2 mixture at 150 °C on carbon sample (spectrum 4) is accompanied by formation of a small band at 1840 cm^{-1} along with another one at 1770 cm^{-1}. Simultaneously, a new IR feature grows in the

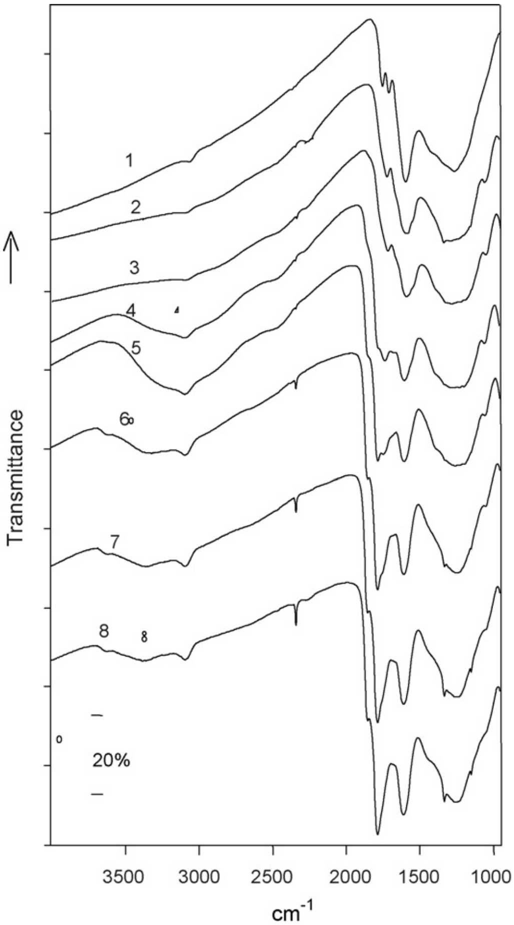

Fig. 5. FT-IR spectra of carbon film exposed to NO + SO_2 in oxygen atmosphere: (1) carbon film after outgassing at 600 °C, (2) after 2 h contact with NO (6.7 Tr) + SO_2 (13.5 Tr) + O_2 (760 Tr) at 25 °C, (3) 100 °C, (4) 150 °C, (5) 200 °C, (6) 250 °C, (7) 300 °C, and (8) 350 °C.

O–H stretching region. During the reaction at 200 °C the intensity of both the 1840 and 1770 cm^{-1} bands sharply increase and the OH– stretching vibrations bands grow in intensity.

Comparing the IR spectra obtained after the NO/O_2 reaction (Fig. 1) to the IR spectra obtained after the $NO/SO_2/O_2$ reaction with carbon (Fig. 5) shows differences in the development and formation of 1253 and 1298 cm^{-1} bands of chelating bridging nitrito species. After the reaction of $NO/SO_2/O_2$ mixture with carbon surface at 200 °C the species responsible for the formation of these bands are not formed on the surface of carbon. Obviously, interaction of SO_2 with the nitrogen containing surface functional groups of carbon took place. Hence, it is concluded that chemisorption of SO_2 may hinder the formation of chelating bridging nitrito species.

The oxidation of SO_2 on carbon surface was greatly enhanced by the presence of NO_2. IR spectroscopic results suggested that NO_2 served as the primary oxidant in the $SO_2/NO/O_2$ exposure.

The uptake of SO_2 by the carbon sample is shown in Fig. 6. The amount of SO_2 adsorbed by the carbon depends strongly on the oxidized atmosphere; i.e. the amount of adsorbed SO_2 increased in the following order: $SO_2 \approx SO_2/NO$, SO_2/O_2, $SO_2/NO/O_2$.

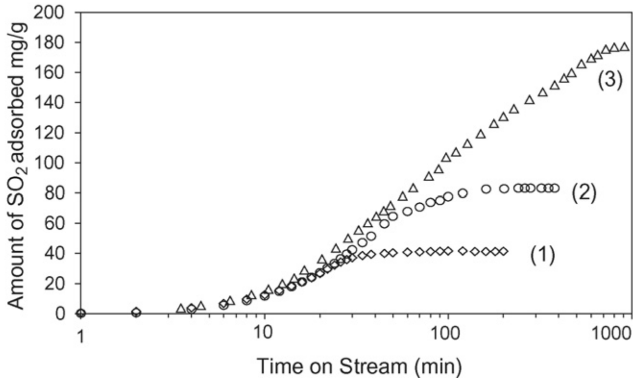

Fig. 6. SO_2 adsorption on carbon sample: (1) SO_2 only, (2) SO_2/O_2, and (3) $SO_2/NO/O_2$. Reaction conditions: m_{cat} 50 mg; total flow rate of the gas mixture 50 ml/min; $[SO_2]_o$ 300 ppm, $[O_2]_o$ 10%, $[NO]_o$ 100 ppm; T 25 °C; Ar was used as a carrier gas.

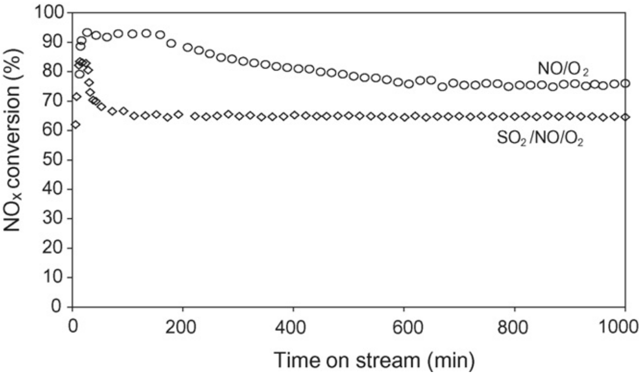

Fig. 7. Conversion of NO_x ($NO + NO_2$) to N_2 over outgassed carbon sample as a function of time on stream. Total flow rate of the gas mixture 50 ml/min; m_{cat} 50 mg; $[NO]_o$ 100 ppm, $[O_2]_o$ 10%; T 25 °C.

Fig. 7 illustrates the conversion of NO_x ($NO + NO_2$) at 25 °C. The steady state conversion for NO/O_2 reaction was ca. 75%. The presence of SO_2 in the gas stream decreased the NO_x conversion to 65%.

Fig. 8 shows the TPD curves obtained with the experimental systems after SO_2 adsorption in the absence and presence of oxidizing agents. When SO_2 reached the adsorption equilibrium, the samples were flushed with Ar within 15 h in order to remove weakly adsorbed or physisorbed SO_2.

Upon heating the sample the evolution of SO_2 (Fig. 8A) and carbon oxides—CO and CO_2 (Fig. 8B) occurs. The results presented in Fig. 8A shows that SO_2 is desorbed mainly at temperatures higher than 200 °C. The line (SO_2) shows two very weak and broad signals of SO_2 centered at 320 and about 500 °C, indicating that it exists in, at least, two different adsorption states. The addition of O_2 into the gas stream (line SO_2/O_2) causes the appearance of the signal at 245 °C.

The SO_2 signals at temperatures above 200 °C are related with strongly adsorbed SO_2 or oxidized to SO_3.

The evolution of oxygen compounds (CO and CO_2) with different thermal stability occurs due to decomposition of surface species (Fig. 8B). Taking into consideration that the sample had been heat treated *in situ* under Ar at 600 °C before

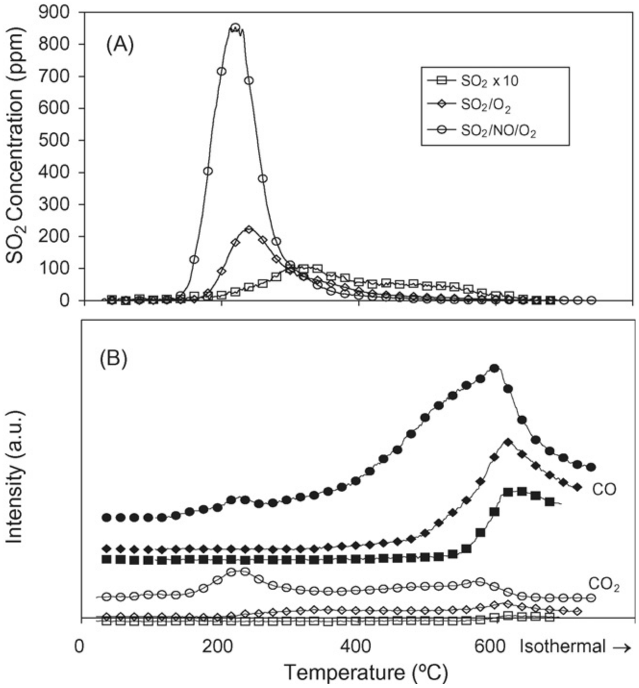

Fig. 8. The TPD profiles of SO_2 (A) and CO/CO_2 (B) after SO_2 adsorption at 25 °C over carbon sample. m_{cat} 50 mg; carrier gas Ar; flow rate 50 ml/min; temperature ramp 5 °C/min. Open symbols in panel (B) CO_2; closed symbols in panel (B) CO.

the adsorption of SO_2, the oxygen complexes must have been formed by the interaction of NO_x with carbon surface. The results presented on Fig. 8B shows that when the carbon sample was put in contact only with SO_2, the CO and CO_2 evolution was quite small. The amount of evolved carbon oxides is much higher after the adsorption process in NO_x atmosphere, in agreement with the greater amount of desorbed SO_2. The formation of C(O) surface complexes are of decisive importance in the low temperature oxidation of SO_2.

The evolution of carbon–oxygen compounds is in agreement with IR spectroscopic results.

The IR spectra show that NO_x conversion is not a pure catalytic process; instead it is also reaction with carbon surface.

These results also suggest that the heterogeneous oxidation of atmospheric SO_2 to sulfate on carbon particles could be significantly influenced by NO_x.

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