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In situ FTIR study of the reduction of NO by H_2 in the presence of O_2 over carbon-film-supported Pt catalyst

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In situ FTIR measurements suggest that the high N_2 selectivity on platinum-loaded oxidized carbon film catalysts depends on the presence of surface nitrite compounds, which were found to be reaction intermediates.

KEY WORDS: carbon films; infrared spectroscopy; nitric oxide reduction; catalytic properties.

1. Introduction

Selective catalytic reduction (SCR) provides a means of reducing the emission of environmentally hazardous nitrogen oxides to N_2 [1–3]. Almost all of the present catalytic deNO_x processes are conducted at temperatures above 300 °C. Increasingly stringent regulations for NO_x emission require the development of efficient catalysts working at lower temperatures. H_2 can reduce NO_x at a low temperature [1,2], and the NO/H_2 reactions

$$2NO + 2H_2 \longrightarrow N_2 + 2H_2O$$

$$2NO + H_2 \longrightarrow N_2O + H_2O$$

$$2NO + 5H_2 \longrightarrow 2NH_3 + 2H_2O$$

have been studied as elementary reactions in catalytic NO_x reduction. In the case of many conventional catalysts the reaction between NO and H_2 is strongly inhibited by O_2 and has been considered only in a few studies [4,5]. These studies describe the reaction on Pt-loaded metal oxide catalysts, including TiO_2, ZrO_2, SiO_2, Al_2O_3, CeO_2 and their composites [6–8].

As far as we know, no reports have been published until now on the intermediate species and reaction mechanism of $NO/H_2/O_2$ reaction on Pt-loaded carbonaceous catalysts using *in situ* FTIR spectroscopy.

2. Experimental

The carbon film ($C_{ox}Pt$) was prepared from cellulose. The raw material used for carbonization was pure cellophane. The charring experiments were set up as follows. Cellulose film was carbonized at 600 °C under dynamic vacuum (0.13 Pa) and then exposed to 100 kPa of pure O_2 at 300 °C and evacuated at 200 °C (0.13 Pa). Pt was loaded from 3% solution of H_2PtCl_6 (pH = 3.75). The IR studies were carried out in a vacuum cell as described previously [9]. For the catalytic tests, the powdered carbon samples were prepared in a similar way. The metal loading level was set as 1 wt%.

The characteristics of the $C_{ox}Pt$ catalyst have been described previously [10]. The material obtained possesses a surface area $S_{DFT} = 587\,m^2/g$ and nearly homogeneous microporosity. The majority of micropores, 88% of the total volume of micropores (determined from DFT, cumulative pore size distribution), possess the same diameter of 0.590 nm.

Steady-state experiments of the $NO/H_2/O_2$ reaction were performed at atmospheric pressure using a fixed-bed down-flow reactor system connected on-line with a multiple-pass IR cell (Sirocco Series Gas Cell, 2 m total pathlength, and volume of 200 cm^3). The samples (0.05 g) were placed in a 4 mm i.d. quartz tube between two layers of glass wool, and the space upstream from the catalyst was pretreated for 1 h at 350 °C in Ar, at a flow rate of 50 ml/min, and cooled to 25 °C in Ar. The reactant gases, 2000 ppm NO in Ar, 4% H_2 in Ar and 40% O_2 in Ar, were supplied through digital mass flow controllers. These gases were mixed to obtain the desired gas composition: 1000 ppm of NO_x (830 ppm of NO, 170 ppm of NO_2), 1% H_2 and 10% O_2 in Ar.

3. Results and discussion

Figure 1 shows the conversion of NO_x ($NO + NO_2$) as well as the N_2 and N_2O selectivity as a function of temperature. We found that the $C_{ox}Pt$ catalyst was active in the NO_x reduction at temperatures as low as 25 °C. The conversion of NO_x at this temperature equaled 53%. The NO_x conversion to N_2/N_2O increased

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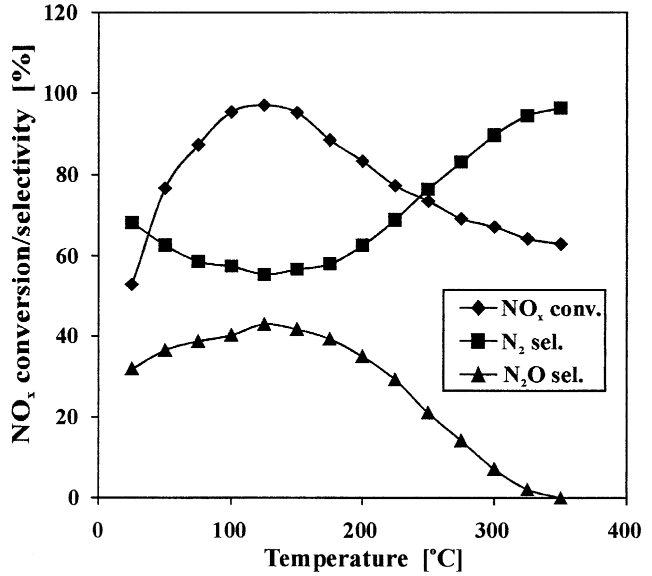

Figure 1. NO conversion and selectivity to N_2 for the $C_{ox}Pt$ catalyst. Reaction conditions: $[NO_x]_o = 1000$ ppm ($[NO]_o = 830$ ppm, $[NO_2]_o = 170$ ppm), $[H_2]_o = 1\%$, $[O_2]_o = 10\%$; total flow rate: 50 ml/min.

with an increase in the temperature, giving rise to a maximum (95%) at ~100 °C. At higher temperatures, however, the NO_x conversion steeply decreased, probably because of competing H_2/O_2 combustion. The selectivity to N_2 slightly decreased from 68% at 25 °C to ~55% at 125 °C and then increased monotonically with an increase in temperature to 96% at 350 °C.

To get a better insight into the processes that are responsible for the observed phenomena, a knowledge of the species present on the surface during the reaction is needed. The IR spectrum of the initial sample (spectrum 1 in figure 2) reveals the presence of absorption bands at 1850, 1780 and 1753 cm^{-1}, which indicates that some of the acidic surface groups of carbon are cyclic anhydrides and probably lactone structures. The results of surface acidity studies of a carbon film have been reported previously [9]. The band at 1600 cm^{-1} is probably due to a C=C stretching mode that is weakly active in the IR because of the breakdown of selection rules. An oxidized layer gives a polyaromatic network enough asymmetry, i.e. the dipole moment changes with vibrations, to make what is basically a C=C mode IR active at 1600 cm^{-1}. Spectra 2–8 in figure 2 show the spectral changes during the $NO/H_2/O_2$ reaction on an oxidized carbon film containing Pt. These spectra are corrected for background by subtracting the $C_{ox}Pt$ spectrum.

After the exposure of $C_{ox}Pt$ to the NO (1.3 kPa) + H_2 (6.7 kPa) + O_2 (93.3 kPa) gas mixture at room temperature, bands of physically adsorbed NO molecules are not observed. During this process quite strong bands at 1732, 1665, 1568, 1342, 1298 and 1254 cm^{-1} appear. These bands arise as a result of the reaction of NO_2 with the carbon film. The bands between 1200 and

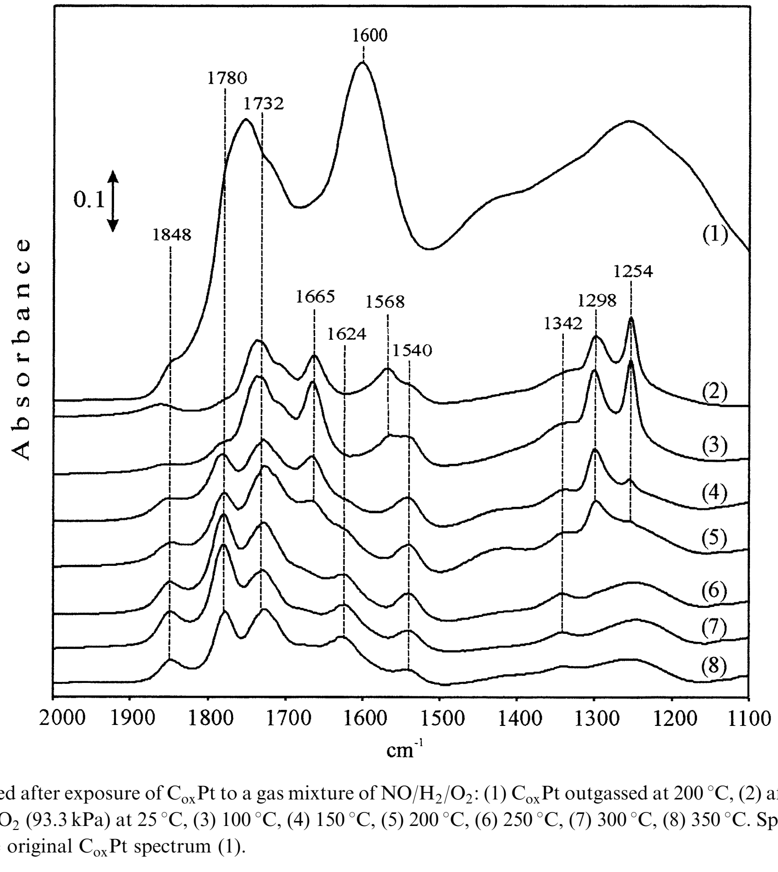

Figure 2. FTIR spectra recorded after exposure of $C_{ox}Pt$ to a gas mixture of $NO/H_2/O_2$: (1) $C_{ox}Pt$ outgassed at 200 °C, (2) after a contact with a gas mixture of NO (1.3 kPa), H_2 (6.7 kPa), O_2 (93.3 kPa) at 25 °C, (3) 100 °C, (4) 150 °C, (5) 200 °C, (6) 250 °C, (7) 300 °C, (8) 350 °C. Spectra 2–8 were corrected for the background by subtracting the original $C_{ox}Pt$ spectrum (1).

1650 cm^{-1} registered after NO_2 adsorption on the surface of different catalysts have been assigned to nitrite and nitro compounds [11,12].

The band at 1665 cm^{-1} can be assigned to the C–O–N=O (chelated) group and the band at 1254 cm^{-1} to the C–O single-bond stretching frequency [12], although the frequency reported for R–O varies widely from one compound to another.

As was reported by Akhter *et al.* [12] the aromatic nitro groups absorb strongly at 1540–1500 cm^{-1} and slightly more weakly at 1370–1310 cm^{-1}. In this work, we found two bands at 1540 and 1342 cm^{-1}, which could be attributed to $C-NO_2$. The bands at 1570 and 1298 cm^{-1} according to the literature [12] could be attributed to $C-NO_2$ in an environment different from the one absorbing at 1540 and 1340 cm^{-1}. While a rise in the reaction temperature causes a decrease and finally disappearance of the N-containing surface compounds, an increase in the intensity of the bands in the region 1700–1850 cm^{-1} is also observed. These bands are because of the increase in surface oxygen complexes, mainly in the form of cyclic anhydrides (1848, 1780 cm^{-1}) and carboxyl surface species [10]. After the reaction at 250 °C (spectrum 6) a band at 1624 cm^{-1} also appears, probably due to adsorbed H_2O.

Taking into consideration the results presented, we can draw a conclusion that the high activity and N_2 selectivity of the $C_{ox}Pt$ sample investigated is closely related to the formation of nitro and nitrite species on the surface. This can be represented as

$$2C + O_2 \longrightarrow 2C(O)$$
$$NO + C(O) \longrightarrow \{C(NO_2)\}$$

Although the adsorbed species of NO on Pt was not detected by IR spectroscopy, dissociative chemisorption probably proceeds on the surface of Pt, producing oxygen and nitrogen atoms [13]:

$$NO_g \longrightarrow NO_{ad} \longrightarrow O_{ad} + N_{ad}$$

The N_{ad} reacting with surface nitro and/or nitrite compounds could produce N_2O:

$$\{C(NO_2)\} + N_{ad} \longrightarrow C(O) + N_2O$$

As long as NO adsorbs in the form of surface $\{C(NO_2)\}$, the latter probably monopolizes the active centers. This limits simple H_2/O_2 combustion in the low-temperature range, where the reaction between surface nitrite species and H_2 should be a rate-determining step. At higher temperatures, however, the increased rate of surface $\{C(NO_2)\}/H_2$ reaction:

$$\{C(NO_2)\} + H_2 \longrightarrow C(O) + H_2O + \tfrac{1}{2}N_2$$

would create a number of vacant active sites available for H_2/O_2 combustion.

4. Conclusions

The data reported in this work show that the carbon-supported Pt catalyst is active in NO reduction by H_2 in the presence of O_2. We have shown that the absolute amount of the reaction products (N_2, N_2O) formed during the reduction of NO by H_2 varies with reaction temperature. The results under our experimental conditions show that NH_3 is not produced (or produced in quantities that are below our detection limit).

The vibrational spectra of NO_x chemisorbed on the surface of the catalyst provide evidence of the participation of surface $\{C(NO_2)\}$ species, which are formed during the process, as the intermediates in the $NO/H_2/O_2$ reaction.

Although it is generally agreed that the presence of oxygen enhances the rate of NO chemisorption on carbon [12,14], the forms of the sorbed species need further investigations.

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