FT-IR spectroscopic investigation of the effect of SO$_2$ on the SCR of NO$_x$ with propene over ZrO$_2$–Nb$_2$O$_5$ catalyst

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**Abstract**
The SO$_2$ tolerance of a catalyst based on ZrO$_2$–Nb$_2$O$_5$ solid solution (mole ratio ZrO$_2$:Nb$_2$O$_5 = 1:6$) in the catalytic activity for NO$_x$ reduction with propene in excess oxygen has been studied. No loss in the C$_3$H$_6$-SCR activity was observed for 2 h after the addition of 56 ppm of SO$_2$ to the reaction mixture. When the concentration of SO$_2$ has been increased to 200 ppm (the so-called fast poisoning experiment) the activity of the catalyst decreased by 13% and remained unchanged for more than 5 h under these conditions. The effect of SO$_2$ on the surface reaction of the SCR reactants has been investigated by in situ FT-IR spectroscopy and mechanism for the suppression of the catalytic activity at high concentration of the poison has been proposed.

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1. Introduction

Selective catalytic reduction of NO$_x$ by hydrocarbons (HC-SCR) has been extensively studied for removal of NO$_x$ from exhaust gases generated by diesel and lean-burn gasoline engines [1–4]. An important factor determining the efficiency of DeNO$_x$ catalysts is their SO$_2$ tolerance. It is assumed that under reaction conditions, the SO$_2$ (which is present in the exhaust) reacts with oxygen to form thermodynamically stable surface sulfates. The latter species cover the catalyst surface and block the sites for NO$_x$ adsorption [5]. Therefore, the development of catalysts resistant to SO$_2$ poisoning is an important task. It has been reported that the deposition of niobium on oxide surfaces such as alumina [6] or zirconia [7] lowers the concentration of basic sites which should result in improved resistance to SO$_2$ poisoning. Recently, we have found that zirconia–niobia solid solution (mole ratio ZrO$_2$:Nb$_2$O$_5 = 6:1$) is active in the selective catalytic reduction of NO$_x$ with propene (C$_3$H$_6$-SCR) in excess oxygen [8]. The conversion of NO$_x$ reaches maximum at 220 °C. Based on in situ FT-IR results, we proposed a reaction mechanism with nitroacetone and NCO species as the key intermediates [8]. In the present work, we investigated the effect of SO$_2$ on the activity of the ZrO$_2$–Nb$_2$O$_5$ solid solution for NO reduction with propene in excess oxygen. The surface reaction of the SCR reactants in the presence of SO$_2$ was monitored by in situ FT-IR spectroscopy.

2. Experimental

Mixed zirconium–niobium oxide was prepared by impregnation of hydrated zirconia with acidic solution (pH ~ 0.5) of peroxoniobium(V) complex, [Nb$_2$(O$_2$)$_3$]$_2$$^{4+}$, ensuring ZrO$_2$:Nb$_2$O$_5$ mole ratio of 6:1. Details about the method of preparation and characterization of the surface acidity are given elsewhere [9]. The BET surface area of the material calcined at 600 °C (denoted as 25NbZ-P) was 42 m$^2$/g. According to XRD the obtained sample has the structure of Zr$_6$Nb$_2$O$_{17}$. The adsorption of 2,6-dimethylpyridine on the 25NbZ-P sample revealed the presence of strong Bronsted acidity.

The equipment and the conditions of catalytic tests of NO$_x$ reduction by propene were described earlier [8]. The conversion degrees of NO$_x$ were taken as a measure of the catalytic activity. The SO$_2$ poisoning experiment was performed with 56 ppm of SO$_2$ in the inlet and under fast poisoning conditions (200 ppm of SO$_2$) at temperature corresponding to the maximum NO$_x$ conversion.

The FT-IR spectra were recorded using a Bomem Hartman & Braun MB-102 model FT-IR spectrometer with a liquid-nitrogen cooled MCT detector at a resolution of 4 cm$^{-1}$ (128 scans). The self-supporting discs (~0.01 g/cm$^2$) were activated in the IR cell by heating for 1 h in a vacuum at 450 °C, and in oxygen (100 mbar, passed through a trap cooled in liquid nitrogen) at the same temperature, followed by evacuation for 1 h at 450 °C. The experiments were carried out under static conditions. The spectra of the
adsorbed compounds were obtained by subtracting the spectra of the activated sample from the spectra recorded. The sample spectra were also gas-phase corrected. The gases NO (99.9%), C3H6 (99.9%) and SO2 (99.9%) used in the in situ FT-IR experiments were supplied by Air Products.

3. Results and discussion

3.1. Catalytic activity in the presence of SO2

We showed earlier [8] that the NOx conversion in the C3H6-SCR reaction over the 25NbZ-P catalyst reaches maximum of 62% at 220 °C and than decreases as the combustion of propene becomes predominant. The conversion of C3H6 is close to 100% at 250 °C. The catalyst displays stable activity at the temperature of maximum NOx conversion (the duration of catalytic activity tests was limited to 10 h). The 25NbZ-P catalyst shows good resistance to SO2 poisoning (Fig. 1). There is no loss in the C3H6-SCR activity for 2 h after the addition of 56 ppm of SO2 to the reaction mixture. When the concentration of SO2 has been increased to 200 ppm (the so-called fast poisoning experiment) the activity of the 25NbZ-P catalyst decreases to approximately 54% of NOx conversion and remains unchanged for more than 5 h under these conditions.

3.2. In situ FT-IR spectroscopic investigations

3.2.1. Co-adsorption of SO2 + O2 over ZrO2 and 25NbZ-P samples

In order to find out the effect of incorporation of Nb(V) into zirconia on the formation of surface SOx species we investigated the adsorption of (0.5 mbar SO2 + 10 mbar O2) mixture on the ZrO2 and 25NbZ-P sample for 15 min at various temperatures. The predominant surface SOx compounds observed in the spectra of zirconia taken below 200 °C are adsorbed SO22− species (the spectra are not shown). The weak band at 1362 cm−1 detected on zirconia at 200 °C (Fig. 2, dotted spectrum (a)) is characteristic of the high-frequency component of the split v3 mode of highly covalent surface sulfates [10,11]. The strong absorption between 1100 and 900 cm−1 (present also in the spectra detected below 200 °C) is attributed to the vibrational modes of SO22− ions coordinated through the S atom to the surface [12,13]. The band at 1000 cm−1 is assigned to the v1 mode, whereas the bands at 1020 and 935 cm−1 correspond to the split v3 stretching vibrations of SO22− ions [12,13]. This assignment is supported by the fact that at 25 °C, the adsorption of 0.5 mbar of SO2 on the zirconia sample causes the appearance of absorptions at 1020, 1000 and 930 cm−1 whose intensities are not affected by

Fig. 1. Results of the SO2 poisoning experiment at 220 °C using 56 and 200 ppm of SO2 in the inlet. (Reaction conditions: 245 ppm NOx, (NO/NO2 = 1.77), 504 ppm C3H6, 9 vol.% O2, GHSV = 10,000 h−1).

Fig. 2. FT-IR spectra collected during the exposure of zirconia (dotted line) and 25NbZ-P sample (solid line) to a (0.5 mbar SO2 + 10 mbar O2) mixture for 10 min at 200 °C (a), 250 °C (b) and 300 °C (c).

Fig. 3. FT-IR spectra of the 25NbZ-P sample collected during the exposure for 10 min to a (2 mbar C3H6 + 6 mbar NO + 4 mbar O2) mixture in the absence (dotted line) and presence of 0.5 mbar SO2 (solid line) at 25 °C (a), 150 °C (b) and 200 °C (c).

The increase in the temperature of the isolated IR cell up to 350 °C. In addition, the band at 1362 cm−1 has not been observed under these conditions (the spectra are not shown).

The heating at 300 °C causes significant increase in the intensity of the sulfite band at 1362 cm−1 at the expense of the absorption corresponding to the sulfate species (Fig. 2, dashed spectrum (c)). The shoulder at 1060 cm−1 is assigned to the low-frequency com-
ponent of the split \( v_3 \) mode of the \( SO_4^{2-} \) groups [10,11]. These results show that noticeable oxidation of \( SO_2 \) over zirconia starts at 300 °C. In this process, most likely, surface oxygen vacancies are involved facilitating the activation of \( O_2 \). Between 200 and 300 °C, the same type of surface \( SO_3 \) species are detected on the 25NbZ-P sample, however with significantly lower concentrations (Fig. 2, solid traces). This indicates that the incorporation of \( Nb^{5+} \) ions into zirconia suppresses the oxidation of \( SO_2 \) to \( SO_3 \).

3.3. Effect of \( SO_2 \) on the \( C_3H_6 + NO + O_2 \) surface reaction

The results of our previous investigation [8] have shown that over the 25NbZ-P sample, characterized by strong Brønsted acidity [9], the activation of propene in the presence of adsorbed \( NO \) species is quite easy at low temperatures, producing surface isopropoxides. The interaction of the latter species with the surface nitrate complexes leads to the formation of nitroacetone. It is proposed [8] that nitroacetone transforms through two parallel reactions. Path (1) involves the basic oxide sites of the catalyst producing acetate species and aci-nitromethane. Path (2) proceeds through the oxidation of nitroacetone to acetates and \( CO_2/H_2O \) with release of \( NO_2 \). The latter process is important at temperatures higher than 200 °C. The aci-nitromethane generates \( NOCO \) species coordinated to the cationic sites of the mixed oxide. The surface isocyanates are detected already at room temperature. It is proposed that the isocyanates react with the \( NO_3^-/NO_2 \) surface complex formed by both oxidation of \( NO \) and oxidation of nitroacetone [8].

Fig. 3 compares the spectra of the 25NbP-Z sample obtained at various temperatures during the adsorption for 15 min of gaseous mixture containing (2 mbar \( C_3H_6 \) + 6 mbar \( NO + 4 \) mbar \( O_2 \)) in the absence (dotted lines) and presence of 0.5 mbar \( SO_2 \) (solid lines). Table 1 gives the assignment of the absorption bands.

The spectra taken at room temperature, contain weak absorption at 2270 cm\(^{-1} \) indicating the formation of \( NCO \) species [8] in both cases, in the presence and absence of \( SO_2 \) (Fig. 3, spectra (a)). The broad band at 1900 cm\(^{-1} \) is characteristic of adsorbed \( N_2O_2 \) [8,11]. Some amounts of adsorbed nitroacetone (1740 cm\(^{-1} \) [8]) and acetone (1680 cm\(^{-1} \) [8]) are observed as well. The difference between both spectra is in the concentration of the surface nitrates (bands at 1655, 1610, 1570, 1277 and 1245 cm\(^{-1} \) [8,11]), which is lower in the presence of \( SO_2 \). In addition, the appearance of bands at 1346 and 1044–1013 cm\(^{-1} \) corresponding to the split \( v_3 \) mode of multidentate \( SO_4^{2-} \) groups coordinated to cationic surface sites [10,11], reveals formation of surface sulfates at room temperature. This indicates that the nitrate species or activated \( NO_2 \) lower significantly the oxidation temperature of \( SO_2 \). Most likely, the sulfate species block the active sites (\( Nb^{5+} \) ions) for the oxidation of \( NO \) to \( NO_2 \) [8] leading to decrease in the concentration of the surface nitrates. As a consequence, the amount of nitroacetone formed at 150 °C in the presence of \( SO_2 \) is lower than that in the absence of the poison (Fig. 3, spectra (b)). The spectrum taken at 200 °C in the presence of \( SO_2 \) (Fig. 3, spectrum (c), solid trace) shows further increase in the amount of sulfate species, which is evident by the enhancement of the absorptions at 1346 and 1044–1013 cm\(^{-1} \). The decrease in the surface concentrations of acetone and nitroacetone at 200 °C measured against the concentrations at 150 °C is considerably smaller than the corresponding decrease observed in the absence of \( SO_2 \) (Fig. 3, compare spectra (b) and (c)). This fact leads to the conclusion that the surface sulfates hinder the transformation of nitroacetone to NCO species. Most likely, the low concentration of nitroacetone and hinderance of its transformation result in lowering the concentration of the NCO species and decrease in the catalyst activity. It should be pointed out that the mechanism proposed for \( SO_2 \) poisoning should operate at high concentration of \( SO_2 \) which is evident from the catalytic activity measurements (see Fig. 1). The results of the investigation show that the catalytic properties of the zirconia–niobia solid solution could be of interest regarding the development of sulfur-tolerant, low-temperature catalysts for the SCR of \( NO_x \) with hydrocarbons.

4. Conclusions

The incorporation of \( Nb(V) \) into zirconia leading to the formation of zirconia–niobia solid solution (mole ratio \( ZrO_2: Nb_2O_5 = 6:1 \)) suppresses the oxidation of \( SO_2 \) to \( SO_3 \). The mixed oxide displays good resistance toward \( SO_2 \) poisoning in the \( C_3H_6-SCR \) of \( NO_x \). No loss in the SCR activity is observed at low concentration of \( SO_2 \) (56 ppm) in the feed gas. The activity declines by 13% at high concentration of the poison (200 ppm) and remains unchanged for more than 5 h. In situ FT-IR investigations show that the nitrate species or activated \( NO_2 \) lower(s) the oxidation temperature of \( SO_2 \) to surface sulfates. The presence of surface \( SO_4^{2-} \) groups decreases the amount of adsorbed nitrates, respectively nitroacetone, and hinders the transformation of the latter compound to NCO species considered as reaction intermediates. This causes decrease in the catalytic activity observed at high concentrations of \( SO_2 \) in the feed gas.

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