



FT-IR spectroscopic investigation of the effect of SO₂ on the SCR of NO_x with propene over ZrO₂–Nb₂O₅ catalyst

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ABSTRACT

The SO₂ tolerance of a catalyst based on ZrO₂–Nb₂O₅ solid solution (mole ratio ZrO₂:Nb₂O₅ = 1:6) in the catalytic activity for NO_x reduction with propene in excess oxygen has been studied. No loss in the C₃H₆-SCR activity was observed 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 catalyst decreased by 13% and remained unchanged for more than 5 h under these conditions. The effect of SO₂ 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 SO₂ tolerance. It is assumed that under reaction conditions, the SO₂ (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 SO₂ 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 SO₂ poisoning. Recently, we have found that zirconia–niobia solid solution (mole ratio ZrO₂:Nb₂O₅ = 6:1) is active in the selective catalytic reduction of NO_x with propene (C₃H₆-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 SO₂ on the activity of the ZrO₂–Nb₂O₅ solid solution for NO reduction with propene in excess oxygen. The surface reaction of the SCR reactants

in the presence of SO₂ 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, [Nb₂(O₂)₃]⁴⁺, ensuring ZrO₂:Nb₂O₅ 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 m²/g. According to XRD the obtained sample has the structure of Zr₆Nb₂O₁₇. The adsorption of 2,6-dimethylpyridine on the 25NbZ-P sample revealed the presence of strong Brønsted 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 SO₂ poisoning experiment was performed with 56 ppm of SO₂ in the inlet and under fast poisoning conditions (200 ppm of SO₂) 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/cm²) 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

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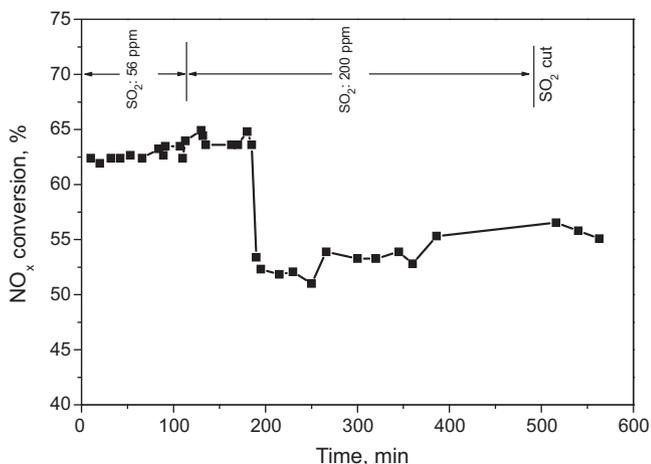


Fig. 1. Results of the SO_2 poisoning experiment at 220°C using 56 and 200 ppm of SO_2 in the inlet. (Reaction conditions: 245 ppm NO_x ($\text{NO}/\text{NO}_2 = 1.77$), 504 ppm C_3H_6 , 9 vol.% O_2 , GHSV = $10,000\text{ h}^{-1}$).

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%), C_3H_6 (99.9%) and SO_2 (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 SO_2

We showed earlier [8] that the NO_x conversion in the C_3H_6 -SCR reaction over the 25NbZ-P catalyst reaches maximum of 62% at 220°C and then decreases as the combustion of propene becomes predominant. The conversion of C_3H_6 is close to 100% at 250°C . The catalyst displays stable activity at the temperature of maximum NO_x conversion (the duration of catalytic activity tests was limited to 10 h). The 25NbZ-P catalyst shows good resistance to SO_2 poisoning (Fig. 1). There is no loss in the C_3H_6 -SCR activity 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 25NbZ-P catalyst decreases to approximately 54% of NO_x 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 $\text{SO}_2 + \text{O}_2$ over ZrO_2 and 25NbZ-P samples

In order to find out the effect of incorporation of Nb(V) into zirconia on the formation of surface SO_x species we investigated the adsorption of (0.5 mbar $\text{SO}_2 + 10\text{ mbar O}_2$) mixture on the ZrO_2 and 25NbZ-P sample for 15 min at various temperatures. The predominant surface SO_x compounds observed in the spectra of zirconia taken below 200°C are adsorbed SO_3^{2-} 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 ν_3 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 SO_3^{2-} ions coordinated through the S atom to the surface [12,13]. The band at 1000 cm^{-1} is assigned to the ν_1 mode, whereas the bands at 1020 and 935 cm^{-1} correspond to the split ν_3 stretching vibrations of SO_3^{2-} ions [12,13]. This assignment is supported by the fact that at 25°C , the adsorption of 0.5 mbar of SO_2 on the zirconia sample causes the appearance of absorptions at 1020 , 1000 and 930 cm^{-1} whose intensities are not affected by

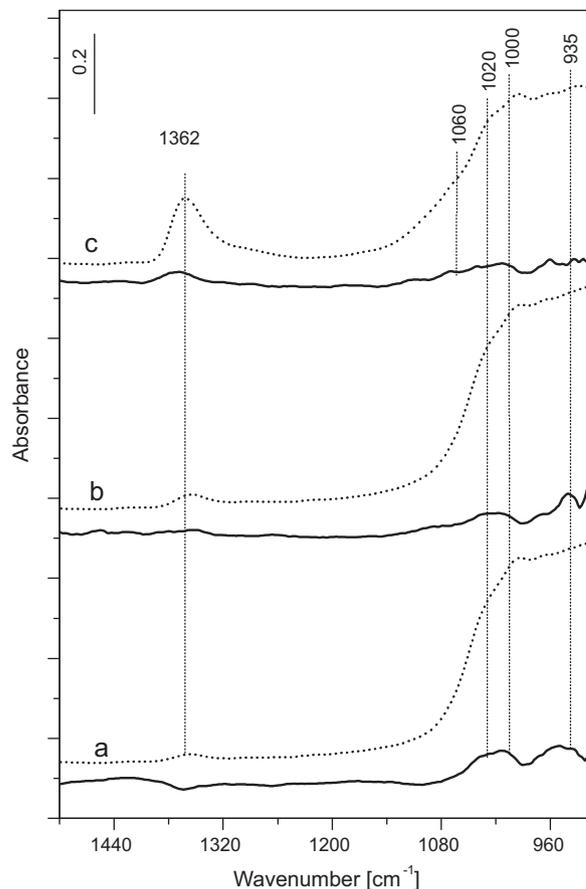


Fig. 2. FT-IR spectra collected during the exposure of zirconia (dotted line) and 25NbZ-P sample (solid line) to a (0.5 mbar $\text{SO}_2 + 10\text{ mbar O}_2$) mixture for 10 min at 200°C (a), 250°C (b) and 300°C (c).

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 sulfate band at 1362 cm^{-1} at the expense of the absorption corresponding to the sulfite species (Fig. 2, dashed spectrum (c)). The shoulder at 1060 cm^{-1} is assigned to the low-frequency com-

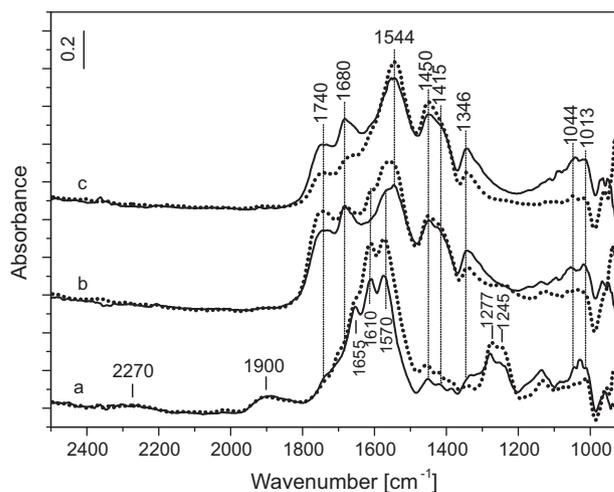


Fig. 3. FT-IR spectra of the 25NbZ-P sample collected during the exposure for 10 min to a (2 mbar $\text{C}_3\text{H}_6 + 6\text{ mbar NO} + 4\text{ mbar O}_2$) mixture in the absence (dotted line) and presence of 0.5 mbar SO_2 (solid line) at 25°C (a), 150°C (b) and 200°C (c).

Table 1

Assignment of the absorption bands in the spectra of 25NbZ-P catalyst observed in the 25–350 °C temperature range during the investigation of the reactivity of surface species formed upon room-temperature adsorption of NO + C₃H₆ + O₂ mixture in the absence and presence of SO₂.

Species	Band position (cm ⁻¹)	Vibration
NCO	2270	$\nu_{as}(\text{NCO})$
N ₂ O ₃ (ads)	1900	$\nu(\text{N=O})$
Nitroacetone (ads)	1740	$\nu(\text{C=O})$
Acetone (ads)	1680	$\nu(\text{C=O})$
Bridged NO ₃ ⁻ (two types)	1655, 1610, 1245	$\nu(\text{N=O}), \nu_{as}(\text{NO}_2)$
Bidentate NO ₃ ⁻	1570, 1275	$\nu(\text{N=O}), \nu_{as}(\text{NO}_2)$
CH ₃ COO ⁻ (two types)	1570, 1544, 1450, 1415, 1346, 1315	$\nu_{as}(\text{COO}), \nu_s(\text{COO}), \delta(\text{CH}_3)$
SO ₄ ²⁻	1346, 1044–1013	$\nu(\text{S=O}), \nu(\text{S-O})$

ponent of the split ν_3 mode of the SO₄²⁻ groups [10,11]. These results show that noticeable oxidation of SO₂ over zirconia starts at 300 °C. In this process, most likely, surface oxygen vacancies are involved facilitating the activation of O₂. Between 200 and 300 °C, the same type of surface SO_x species are detected on the 25NbZ-P sample, however with significantly lower concentrations (Fig. 2, solid traces). This indicates that the incorporation of Nb⁵⁺ ions into zirconia suppresses the oxidation of SO₂ to SO₃.

3.3. Effect of SO₂ on the C₃H₆ + NO + O₂ 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_x 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 oxidation of nitroacetone to acetates and CO_x/H₂O with release of NO₂. The latter process is important at temperatures higher than 200 °C. The aci-nitromethane generates NCO 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 NO₃⁻/NO₂ surface complex formed by both oxidation of NO and oxidation of nitroacetone [8].

Fig. 3 compares the spectra of the 25NbZ-P sample obtained at various temperatures during the adsorption for 15 min of gaseous mixture containing (2 mbar C₃H₆ + 6 mbar NO + 4 mbar O₂) in the absence (dotted lines) and presence of 0.5 mbar SO₂ (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 SO₂ (Fig. 3, spectra (a)). The broad band at 1900 cm⁻¹ is characteristic of adsorbed N₂O₃ [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 SO₂. In addition, the appearance of bands at 1346 and 1044–1013 cm⁻¹ corresponding to the split ν_3 mode of multidentate SO₄²⁻ groups coordinated to cationic surface sites [10,11], reveals formation of surface sulfates at room temperature. This indicates that the nitrate species or activated NO₂ lower significantly the oxidation temperature of SO₂. Most likely, the sulfate species block the active sites (Nb⁵⁺ ions) for the oxidation of NO to NO₂ [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 SO₂ is lower than that in the absence of the poison (Fig. 3, spectra (b)). The spectrum taken at 200 °C in the

presence of SO₂ (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 SO₂ (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 hindrance 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 SO₂ poisoning should operate at high concentration of SO₂ 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 ZrO₂:Nb₂O₅ = 6:1) suppresses the oxidation of SO₂ to SO₃. The mixed oxide displays good resistance toward SO₂ poisoning in the C₃H₆-SCR of NO_x. No loss in the SCR activity is observed at low concentration of SO₂ (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 NO₂ lower(s) the oxidation temperature of SO₂ to surface sulfates. The presence of surface SO₄²⁻ 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 SO₂ in the feed gas.

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