



# FT-IR spectroscopic investigation of the effect of SO<sub>2</sub> on the SCR of NO<sub>x</sub> with propene over ZrO<sub>2</sub>–Nb<sub>2</sub>O<sub>5</sub> catalyst

M. Kantcheva<sup>a,\*</sup>, I. Cayirtepe<sup>a</sup>, A. Naydenov<sup>b</sup>, G. Ivanov<sup>b</sup>

<sup>a</sup> Department of Chemistry, Bilkent University, 06800 Bilkent, Ankara, Turkey

<sup>b</sup> Institute of General and Inorganic Chemistry, BAS, Sofia 1113, Bulgaria

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In situ FT-IR spectroscopy

Mechanism of SO<sub>2</sub> poisoning

## ABSTRACT

The SO<sub>2</sub> tolerance of a catalyst based on ZrO<sub>2</sub>–Nb<sub>2</sub>O<sub>5</sub> solid solution (mole ratio ZrO<sub>2</sub>:Nb<sub>2</sub>O<sub>5</sub> = 1:6) in the catalytic activity for NO<sub>x</sub> reduction with propene in excess oxygen has been studied. No loss in the C<sub>3</sub>H<sub>6</sub>-SCR activity was observed for 2 h after the addition of 56 ppm of SO<sub>2</sub> to the reaction mixture. When the concentration of SO<sub>2</sub> 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<sub>2</sub> 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<sub>x</sub> by hydrocarbons (HC-SCR) has been extensively studied for removal of NO<sub>x</sub> from exhaust gases generated by diesel and lean-burn gasoline engines [1–4]. An important factor determining the efficiency of DeNO<sub>x</sub> catalysts is their SO<sub>2</sub> tolerance. It is assumed that under reaction conditions, the SO<sub>2</sub> (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<sub>x</sub> adsorption [5]. Therefore, the development of catalysts resistant to SO<sub>2</sub> 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<sub>2</sub> poisoning. Recently, we have found that zirconia–niobia solid solution (mole ratio ZrO<sub>2</sub>:Nb<sub>2</sub>O<sub>5</sub> = 6:1) is active in the selective catalytic reduction of NO<sub>x</sub> with propene (C<sub>3</sub>H<sub>6</sub>-SCR) in excess oxygen [8]. The conversion of NO<sub>x</sub> 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<sub>2</sub> on the activity of the ZrO<sub>2</sub>–Nb<sub>2</sub>O<sub>5</sub> solid solution for NO reduction with propene in excess oxygen. The surface reaction of the SCR reactants

in the presence of SO<sub>2</sub> was monitored by in situ FT-IR spectroscopy.

## 2. Experimental

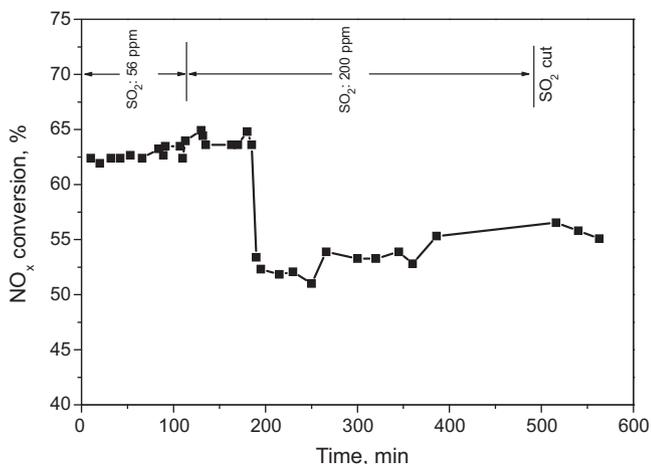
Mixed zirconium–niobium oxide was prepared by impregnation of hydrated zirconia with acidic solution (pH ~ 0.5) of peroxoniobium(V) complex, [Nb<sub>2</sub>(O<sub>2</sub>)<sub>3</sub>]<sup>4+</sup>, ensuring ZrO<sub>2</sub>:Nb<sub>2</sub>O<sub>5</sub> mole ratio of 6:1. Details about the method of preparation 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<sup>2</sup>/g. According to XRD the obtained sample has the structure of Zr<sub>6</sub>Nb<sub>2</sub>O<sub>17</sub>. 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<sub>x</sub> reduction by propene were described earlier [8]. The conversion degrees of NO<sub>x</sub> were taken as a measure of the catalytic activity. The SO<sub>2</sub> poisoning experiment was performed with 56 ppm of SO<sub>2</sub> in the inlet and under fast poisoning conditions (200 ppm of SO<sub>2</sub>) at temperature corresponding to the maximum NO<sub>x</sub> 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<sup>-1</sup> (128 scans). The self-supporting discs (~0.01 g/cm<sup>2</sup>) 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

\* Corresponding author. Tel.: +90 312 290 2451; fax: +90 312 266 4068.

E-mail address: [margi@fen.bilkent.edu.tr](mailto:margi@fen.bilkent.edu.tr) (M. Kantcheva).



**Fig. 1.** Results of the  $\text{SO}_2$  poisoning experiment at  $220^\circ\text{C}$  using 56 and 200 ppm of  $\text{SO}_2$  in the inlet. (Reaction conditions: 245 ppm  $\text{NO}_x$  ( $\text{NO}/\text{NO}_2 = 1.77$ ), 504 ppm  $\text{C}_3\text{H}_6$ , 9 vol.%  $\text{O}_2$ , 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  $\text{NO}$  (99.9%),  $\text{C}_3\text{H}_6$  (99.9%) and  $\text{SO}_2$  (99.9%) used in the in situ FT-IR experiments were supplied by Air Products.

### 3. Results and discussion

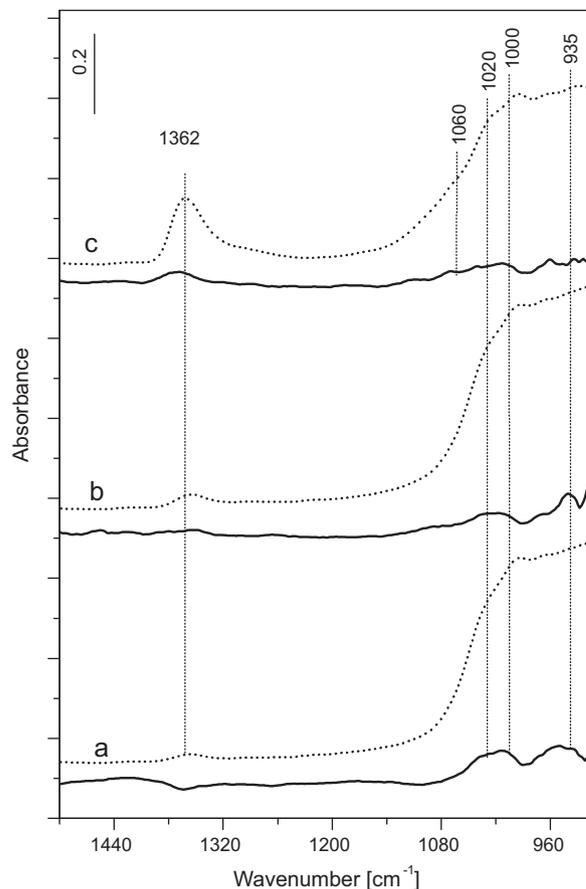
#### 3.1. Catalytic activity in the presence of $\text{SO}_2$

We showed earlier [8] that the  $\text{NO}_x$  conversion in the  $\text{C}_3\text{H}_6$ -SCR reaction over the 25NbZ-P catalyst reaches maximum of 62% at  $220^\circ\text{C}$  and then decreases as the combustion of propene becomes predominant. The conversion of  $\text{C}_3\text{H}_6$  is close to 100% at  $250^\circ\text{C}$ . The catalyst displays stable activity at the temperature of maximum  $\text{NO}_x$  conversion (the duration of catalytic activity tests was limited to 10 h). The 25NbZ-P catalyst shows good resistance to  $\text{SO}_2$  poisoning (Fig. 1). There is no loss in the  $\text{C}_3\text{H}_6$ -SCR activity for 2 h after the addition of 56 ppm of  $\text{SO}_2$  to the reaction mixture. When the concentration of  $\text{SO}_2$  has been increased to 200 ppm (the so-called fast poisoning experiment) the activity of the 25NbZ-P catalyst decreases to approximately 54% of  $\text{NO}_x$  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 $\text{ZrO}_2$ and 25NbZ-P samples

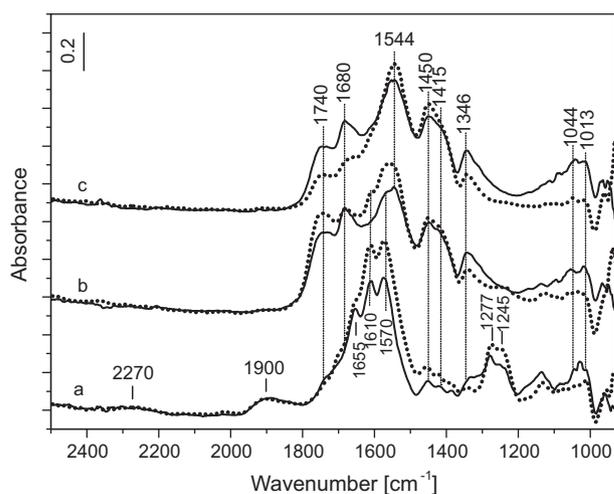
In order to find out the effect of incorporation of Nb(V) into zirconia on the formation of surface  $\text{SO}_x$  species we investigated the adsorption of (0.5 mbar  $\text{SO}_2 + 10\text{ mbar O}_2$ ) mixture on the  $\text{ZrO}_2$  and 25NbZ-P sample for 15 min at various temperatures. The predominant surface  $\text{SO}_x$  compounds observed in the spectra of zirconia taken below  $200^\circ\text{C}$  are adsorbed  $\text{SO}_3^{2-}$  species (the spectra are not shown). The weak band at  $1362\text{ cm}^{-1}$  detected on zirconia at  $200^\circ\text{C}$  (Fig. 2, dotted spectrum (a)) is characteristic of the high-frequency component of the split  $\nu_3$  mode of highly covalent surface sulfates [10,11]. The strong absorption between  $1100$  and  $900\text{ cm}^{-1}$  (present also in the spectra detected below  $200^\circ\text{C}$ ) is attributed to the vibrational modes of  $\text{SO}_3^{2-}$  ions coordinated through the S atom to the surface [12,13]. The band at  $1000\text{ cm}^{-1}$  is assigned to the  $\nu_1$  mode, whereas the bands at  $1020$  and  $935\text{ cm}^{-1}$  correspond to the split  $\nu_3$  stretching vibrations of  $\text{SO}_3^{2-}$  ions [12,13]. This assignment is supported by the fact that at  $25^\circ\text{C}$ , the adsorption of 0.5 mbar of  $\text{SO}_2$  on the zirconia sample causes the appearance of absorptions at  $1020$ ,  $1000$  and  $930\text{ cm}^{-1}$  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  $200^\circ\text{C}$  (a),  $250^\circ\text{C}$  (b) and  $300^\circ\text{C}$  (c).

the increase in the temperature of the isolated IR cell up to  $350^\circ\text{C}$ . In addition, the band at  $1362\text{ cm}^{-1}$  has not been observed under these conditions (the spectra are not shown).

The heating at  $300^\circ\text{C}$  causes significant increase in the intensity of the sulfate band at  $1362\text{ cm}^{-1}$  at the expense of the absorption corresponding to the sulfite species (Fig. 2, dashed spectrum (c)). The shoulder at  $1060\text{ cm}^{-1}$  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  $\text{SO}_2$  (solid line) at  $25^\circ\text{C}$  (a),  $150^\circ\text{C}$  (b) and  $200^\circ\text{C}$  (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 + C<sub>3</sub>H<sub>6</sub> + O<sub>2</sub> mixture in the absence and presence of SO<sub>2</sub>.

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

ponent of the split  $\nu_3$  mode of the SO<sub>4</sub><sup>2-</sup> groups [10,11]. These results show that noticeable oxidation of SO<sub>2</sub> over zirconia starts at 300 °C. In this process, most likely, surface oxygen vacancies are involved facilitating the activation of O<sub>2</sub>. Between 200 and 300 °C, the same type of surface SO<sub>x</sub> species are detected on the 25NbZ-P sample, however with significantly lower concentrations (Fig. 2, solid traces). This indicates that the incorporation of Nb<sup>5+</sup> ions into zirconia suppresses the oxidation of SO<sub>2</sub> to SO<sub>3</sub>.

### 3.3. Effect of SO<sub>2</sub> on the C<sub>3</sub>H<sub>6</sub> + NO + O<sub>2</sub> 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<sub>x</sub> 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<sub>x</sub>/H<sub>2</sub>O with release of NO<sub>2</sub>. 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 NO<sub>3</sub><sup>-</sup>/NO<sub>2</sub> 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 C<sub>3</sub>H<sub>6</sub> + 6 mbar NO + 4 mbar O<sub>2</sub>) in the absence (dotted lines) and presence of 0.5 mbar SO<sub>2</sub> (solid lines). Table 1 gives the assignment of the absorption bands.

The spectra taken at room temperature, contain weak absorption at 2270 cm<sup>-1</sup> indicating the formation of NCO species [8] in both cases, in the presence and absence of SO<sub>2</sub> (Fig. 3, spectra (a)). The broad band at 1900 cm<sup>-1</sup> is characteristic of adsorbed N<sub>2</sub>O<sub>3</sub> [8,11]. Some amounts of adsorbed nitroacetone (1740 cm<sup>-1</sup> [8]) and acetone (1680 cm<sup>-1</sup> [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<sup>-1</sup> [8,11]), which is lower in the presence of SO<sub>2</sub>. In addition, the appearance of bands at 1346 and 1044–1013 cm<sup>-1</sup> corresponding to the split  $\nu_3$  mode of multidentate SO<sub>4</sub><sup>2-</sup> 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<sub>2</sub> lower significantly the oxidation temperature of SO<sub>2</sub>. Most likely, the sulfate species block the active sites (Nb<sup>5+</sup> ions) for the oxidation of NO to NO<sub>2</sub> [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<sub>2</sub> 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<sub>2</sub> (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<sup>-1</sup>. 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<sub>2</sub> (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 SO<sub>2</sub> poisoning should operate at high concentration of SO<sub>2</sub> 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<sub>x</sub> with hydrocarbons.

## 4. Conclusions

The incorporation of Nb(V) into zirconia leading to the formation of zirconia–niobia solid solution (mole ratio ZrO<sub>2</sub>:Nb<sub>2</sub>O<sub>5</sub> = 6:1) suppresses the oxidation of SO<sub>2</sub> to SO<sub>3</sub>. The mixed oxide displays good resistance toward SO<sub>2</sub> poisoning in the C<sub>3</sub>H<sub>6</sub>-SCR of NO<sub>x</sub>. No loss in the SCR activity is observed at low concentration of SO<sub>2</sub> (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<sub>2</sub> lower(s) the oxidation temperature of SO<sub>2</sub> to surface sulfates. The presence of surface SO<sub>4</sub><sup>2-</sup> 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<sub>2</sub> in the feed gas.

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