

# Characterization of $Zr_6Nb_2O_{17}$ synthesized by a peroxy route as a novel solid acid

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## Abstract

The impregnation of hydrated zirconia at pH  $\sim 0.5$  with a solution of peroxoniobium(V) complex,  $[Nb_2(O_2)_3]^{4+}$ , ensuring a  $ZrO_2:Nb_2O_5$  mole ratio of 6:1 followed by calcination at 873 K resulted in the formation of a  $Zr_6Nb_2O_{17}$  solid solution. The structure of this compound was confirmed by XRD. The surface acidity was investigated by in situ FT-IR spectroscopy using 2,6-dimethylpyridine (lutidine).  $Zr_6Nb_2O_{17}$  has a sufficient amount of Brønsted acid sites necessary for the stabilization of dispersed Pd(II) species. The potential of the Pd-promoted  $Zr_6Nb_2O_{17}$  as a catalyst for the reduction of NO with methane was evaluated by studying the reactivity of adsorbed  $NO_x$  species toward the hydrocarbon.

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**Keywords:**  $Zr_6Nb_2O_{17}$ ; Synthesis from niobium(V) peroxy precursor; Surface acidity; Pd promotion;  $CH_4$ -SCR mechanism

## 1. Introduction

Niobium-based materials show potential applications in various oxidation and acid-catalyzed reactions [1,2]. Niobium pentoxide can be used as a promoter, support and an active phase [1,2]. Supported niobia catalysts have been extensively studied as solid acids [3–7]. Turek and Wachs [4] suggested that the bridging Nb–O–M bonds (M = support cation) are responsible for the acidic properties of these materials. It has been shown [8] that the deposition of  $WO_x$  species on hydrated zirconia from an acidic hydrogen peroxide medium (the so called “peroxy route”) leads to the appearance of a substantial amount of Zr-containing polytungstates giving rise to high permanent Brønsted acidity in the calcined material. Niobium(V) ions can react with hydrogen peroxide at a low pH producing niobium(V) peroxide complexes [9,10]. Here, we report the results of the surface characterization of Pd-free and Pd-promoted

$Nb_2O_5$ – $ZrO_2$  solid solution,  $Zr_6Nb_2O_{17}$ , obtained by the impregnation of hydrated zirconia with an acidic solution of the peroxoniobium(V) complex,  $[Nb_2(O_2)_3]^{4+}$ . The formation of a series of  $ZrO_2$ – $Nb_2O_5$  solid solutions, with  $ZrO_2:Nb_2O_5$  mole ratios ranging from 5.1:1 to 10:1, by a ceramic process from mixtures of zirconia and niobia powders at temperatures exceeding 1270 K has been reported in the literature [11]. Kominami et al. [12] obtained a single phase of  $Zr_6Nb_2O_{17}$  directly by a glycothermal method. Recently, Lu et al. [13] synthesized crystallized mesoporous  $Zr_6Nb_2O_{17}$  using block copolymer surfactant and chlorides of Zr(IV) and Nb(V). To the best of our knowledge, there are no reports dealing with the surface acidity of this material and its potential as a catalyst.

## 2. Experimental

### 2.1. Sample preparation

Amorphous  $ZrO_x(OH)_{4-2x}$  was prepared by the hydrolysis of  $ZrCl_4$  (Merck, for synthesis) with a concentrated (25%) solution of ammonia.

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A solution of the complex  $[\text{Nb}_2(\text{O}_2)_3]^{4+}$  was prepared according to the procedure described in Ref. [10]. The starting Nb(V) precursor,  $(\text{NH}_4)(\text{C}_2\text{O}_4)_2\text{NbO} \cdot x\text{H}_2\text{O}$  (Aldrich,  $x = 19.15$ ), was added under stirring in small portions to a 30%  $\text{H}_2\text{O}_2$  solution (Merck, without stabilizer) acidified to a pH  $\sim 0.5$  by concentrated  $\text{HNO}_3$  and then the solution was heated for 1 h at 323 K. The color of the resulting solution was yellow exhibiting a UV absorption band at 335 nm typical of a complex with a peroxo:Nb mole ratio of 3:2 [9]. Hydrated zirconia was impregnated for 24 h, under stirring, at room temperature with the peroxoniobium(V) solution taken in concentration ensuring a mole ratio  $\text{ZrO}_2:\text{Nb}_2\text{O}_5 = 6:1$ . The amount of the hydrated zirconia was determined according to the weight loss after the calcination for 2 h at 873 K. The liquid was removed from the suspension by gentle evaporation at 343 K and the solid was calcined under static air for 2 h at 623 K and 2 h at 873 K (heating rate 10 K/min). The sample obtained from the niobium(V) peroxo precursor is denoted as NbZ-P. The BET surface area of the calcined material is  $42 \text{ m}^2/\text{g}$ . The deposition of Pd(II) was performed by impregnation of the calcined NbZ-P sample with an aqueous solution of  $\text{Pd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  (Merck) giving 0.1 wt% of nominal palladium content followed by drying at 343 K and calcination under static air for 2 h at 773 K. This sample is labeled as 0.1Pd/NbZ-P.

For comparison purposes a  $\text{Nb}_2\text{O}_5\text{--ZrO}_2$  sample containing the same  $\text{ZrO}_2:\text{Nb}_2\text{O}_5$  mole ratio was synthesized by impregnating hydrated zirconia with an aqueous solution of ammonium niobium oxalate. This sample (labeled as NbZ-O) was dried and calcined according to the procedures described above. Niobium pentoxide was obtained by the precipitation of  $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$  with a concentrated (25%) solution of ammonia from an aqueous solution of ammonium niobium oxalate at pH 8.2. The precipitate was separated from the solution, washed with deionized water (negative test for oxalate ions) and calcined for 2 h at 873 K. Monoclinic zirconia was obtained by the calcination of hydrated zirconium oxyhydroxide at 873 K for 2 h.

## 2.2. Characterization techniques

The XRD analysis was performed on a Rigaku Miniflex diffractometer with Ni-filtered  $\text{Cu K}\alpha$  radiation under ambient conditions. DR-UV–vis spectra were obtained under ambient conditions with a fiber optic spectrometer AvaSpec-2048 (Avantes) using WS-2 as a reference.

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  $4 \text{ cm}^{-1}$  (128 scans). The self-supporting discs ( $\sim 0.01 \text{ g}/\text{cm}^2$ ) were activated in the IR cell by heating for 1 h in a vacuum at 723 K, and in oxygen (100 mbar, passed through a trap cooled in liquid nitrogen) at the same temperature, followed by evacuation for 1 h at 723 K. The surface acidity of the samples was investigated by in situ FT-IR spectroscopy using 2,6-dimethylpyridine (lutidine) and NO as

probe molecules. The 2,6-dimethylpyridine (lutidine, Sigma–Aldrich, redistilled) adsorption test was carried out by the admission of 2.5 mbar of the base into the IR cell and left in contact with the sample for 10 min. The excess 2,6-lutidine was then evacuated at room temperature for 15 min, followed by a desorption of the strongly bonded base fraction in the temperature range 150–723 K. The purity of the NO gas (Air Products) was 99.9%. The spectra of the adsorbed compounds were obtained by subtracting the spectra of the activated samples from the spectra recorded.

## 3. Results and discussion

### 3.1. Structural characterization of the $\text{Nb}_2\text{O}_5\text{--ZrO}_2$ samples

Fig. 1 compares the XRD patterns of niobia with those of the  $\text{Nb}_2\text{O}_5\text{--ZrO}_2$  samples. The crystallographic modification of  $\text{Nb}_2\text{O}_5$  synthesized corresponds to the pseudo-hexagonal TT-phase (ICDD Card No. 27-1312). The XRD patterns of the NbZ-O sample revealed the presence of two phases – niobia and tetragonal zirconia. All diffraction peaks of the NbZ-P sample are indexed as  $\text{Zr}_6\text{Nb}_2\text{O}_{17}$  (ICDD card No 09-0251). The average crystallite size is 19 nm as determined by the Scherrer equation using the (111) peak at  $2\theta = 30.0^\circ$  in the diffractogram of  $\text{Zr}_6\text{Nb}_2\text{O}_{17}$ . No signals of the other phases are observed. The Raman spectrum of the NbZ-P sample (not shown)

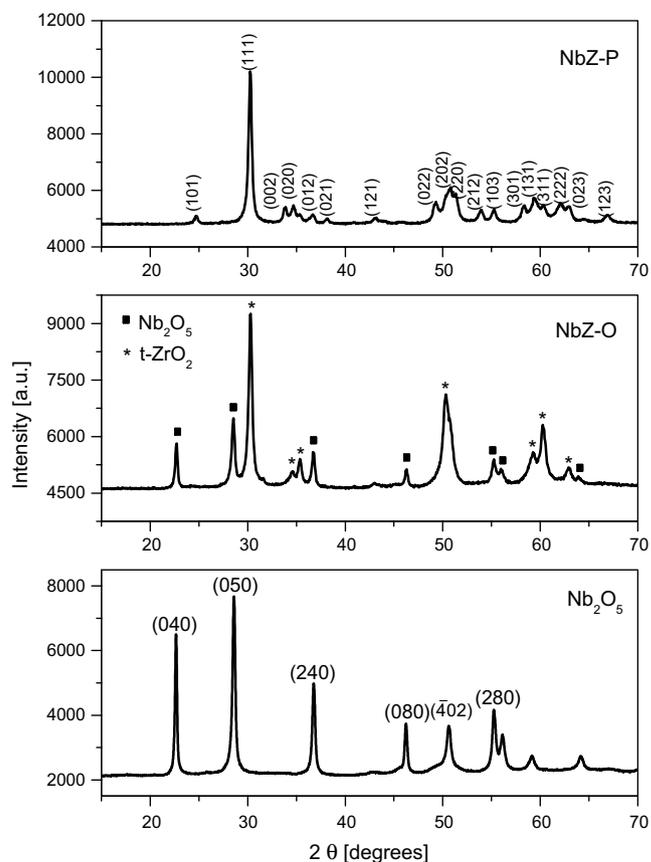


Fig. 1. XRD patterns of the samples studied.

does not contain bands characteristic of crystalline  $\text{Nb}_2\text{O}_5$  which confirms the formation of a single phase of  $\text{Zr}_6\text{Nb}_2\text{O}_{17}$ . This is in agreement with the fact that the structure of  $\text{Nb}_2\text{Zr}_{x-2}\text{O}_{2x+1}$  solid solutions ( $x = 7.1\text{--}12$ ) is described as a superstructure made up of subcells of metal and oxygen atoms allowing the accommodation of various Nb concentrations [11]. The formation of the  $\text{Zr}_6\text{Nb}_2\text{O}_{17}$  is favored by the partial solubility of hydrous zirconia in  $\text{H}_2\text{O}_2$  solution [8].

### 3.2. Brønsted acidity of $\text{Zr}_6\text{Nb}_2\text{O}_{17}$

The FT-IR spectra of the activated samples in the  $\nu(\text{OH})$  stretching region are shown in Fig. 2a. The  $\text{ZrO}_2$  sample (monoclinic) is completely dehydroxylated after the activation procedure is employed. In contrast, the NbZ-P sample exhibits a wide signal, which extends down to  $2400\text{ cm}^{-1}$ . This absorption is ascribed to the  $\nu(\text{OH})$  stretching vibrations of H-bonded surface hydroxyls of  $\text{Zr}_6\text{Nb}_2\text{O}_{17}$ .

The Brønsted acidity of  $\text{Zr}_6\text{Nb}_2\text{O}_5$  has been tested by the adsorption of lutidine. This probe molecule, because of its higher basicity and steric hindrance of the methyl groups, is more sensitive to Brønsted acidity than pyridine [14,15]. Fig. 2b compares the spectra of  $\text{ZrO}_2$  and  $\text{Zr}_6\text{Nb}_2\text{O}_5$  obtained after the admission of 2.5 mbar of the base followed by evacuation for 15 min at 423 K. The weak unresolved absorption at approximately  $1610\text{ cm}^{-1}$  and the band at  $1567\text{ cm}^{-1}$  detected on zirconia characterize lutidine adducts with the Lewis acid sites [6,15,16] and are due to the 8a and 8b modes of the coordinated base, respectively. The strong bands at 1643 and  $1628\text{ cm}^{-1}$  observed in the spectrum of the NbZ-P samples correspond to the 8a and 8b vibrational modes, respectively, of protonated lutidine species (lutidinium cation) [6,15,16] and testify the existence of Brønsted acid sites on the surface of  $\text{Zr}_6\text{Nb}_2\text{O}_{17}$ . The species at 1643 and  $1628\text{ cm}^{-1}$  are strongly held and resist the evacuation at 723 K.

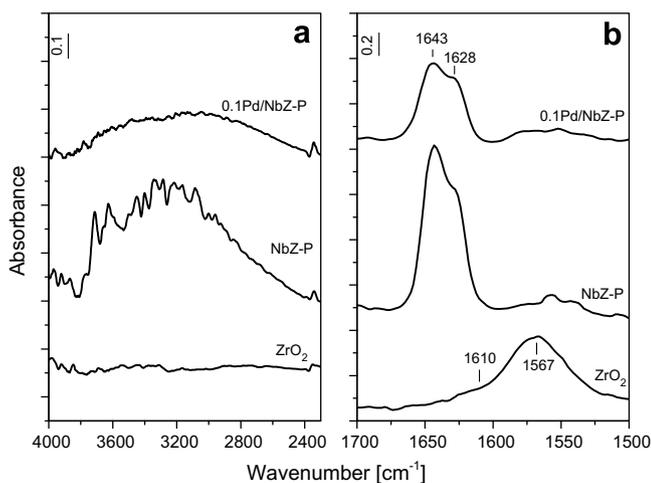


Fig. 2. (a) FT-IR spectra of the activated samples. (b) FT-IR spectra of lutidine (2.5 mbar) adsorbed at room temperature for 10 min followed by evacuation at 423 K for 15 min.

### 3.3. Pd-promoted $\text{Zr}_6\text{Nb}_2\text{O}_{17}$ solid solution

#### 3.3.1. Brønsted acidity

Resasco and coworkers [17–19] concluded that the Brønsted acid sites of anion-modified zirconias play an important role in stabilizing the Pd(II) species in a highly dispersed state. The promotion of the NbZ-P sample with palladium causes a strong erosion of the absorption in the  $\nu(\text{OH})$  stretching region (Fig. 2a) which indicates that  $\text{Pd}^{2+}$  ions replace protons of the surface hydroxyls. This results in a corresponding decrease in the amount of Brønsted acid sites on the Pd/NbZ-P sample (Fig. 2b).

#### 3.3.2. DR-UV–vis spectroscopy

The DR-UV–vis spectrum of the 0.1Pd/NbZ-P sample is shown in Fig. 3. The band at 325 nm corresponds to  $\text{O}^{2-} \rightarrow \text{Nb}^{5+}$  charge transfer transition [5,6]. The absorption at  $\sim 420\text{ nm}$  is attributed to d–d transition of either isolated  $\text{Pd}^{2+}$  ions linked to surface oxygen atoms of the support, or small  $\text{Pd}(\text{O})_n^{2+}$  entities [20,21].

#### 3.3.3. Adsorption of NO at room temperature

The existence of Pd(II) species in a dispersed state on the surface of  $\text{Zr}_6\text{Nb}_2\text{O}_{17}$  has been confirmed by adsorption of NO (8 mbar) at room temperature (Fig. 4). The bands at 1859 and  $1815\text{ cm}^{-1}$  detected on the NbZ-P sample are typical of two types of coordinatively unsaturated  $\text{Pd}^{2+}$  ions differing in their environment [18,19,21]. These bands are stable upon NO evacuation. The bare NbZ-P sample shows a band at  $1925\text{ cm}^{-1}$  which is removed by room temperature evacuation of NO. Based on the analysis of the low-frequency region, this signal is attributed to the  $\nu(\text{N}=\text{O})$  mode of adsorbed  $\text{N}_2\text{O}_3$  [21]. The absorptions at 1859

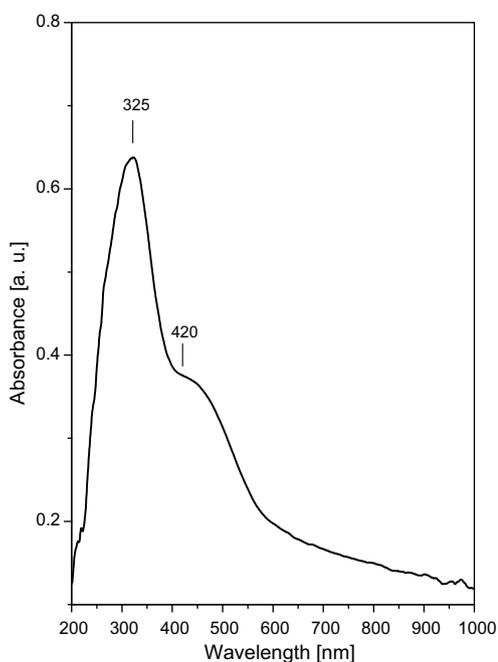


Fig. 3. DR-UV–vis spectrum of the 0.1Pd/NbZ-P sample.

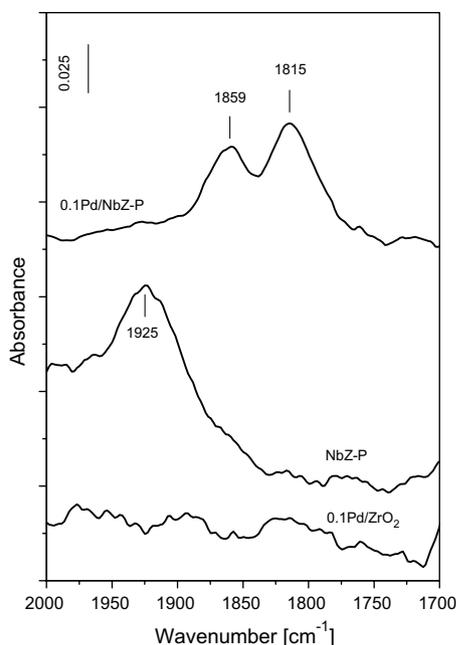


Fig. 4. FT-IR spectra of adsorbed NO (8 mbar) at room temperature.

and  $1815\text{ cm}^{-1}$  are not observed for the  $0.1\text{Pd}/\text{ZrO}_2$  sample despite the fact that both  $0.1\text{Pd}/\text{NbZ-P}$  and  $0.1\text{Pd}/\text{ZrO}_2$  samples contain the same amount of Pd. This result is in line with the conclusion made by Resasco and coworkers [18] that materials lacking Brønsted acidity (such as  $\text{ZrO}_2$ ) do not have the ability to stabilize dispersed Pd(II) species. The formation of Pd(II) nitrosyls on the  $0.1\text{Pd}/\text{NbZ-P}$  sample may be ascribed to the particle size effect,

as smaller  $\text{Pd}(\text{O})_n^{2+}$  particles should exhibit a higher fraction of coordinatively unsaturated cationic sites.

### 3.4. Reactivity of $\text{NO}_x$ species adsorbed on $0.1\text{Pd}/\text{Zr}_6\text{Nb}_2\text{O}_{17}$ toward methane

Low-loading palladium catalysts supported on anion-modified zirconias exhibit high activity and selectivity in the reduction of NO with methane in the presence of oxygen [17,19]. Since we cannot report catalytic data, we tested the potential of the  $0.1\text{Pd}/\text{NbZ-P}$  sample as a catalyst for the  $\text{CH}_4$ -SCR of NO by studying the reactivity of adsorbed  $\text{NO}_x$  species toward methane. The detection of reactive intermediates leading to the  $\text{CH}_4$ -SCR products can be used as evidence that this material should be active in the catalytic reduction of NO with methane.

Surface  $\text{NO}_x$  species were created by room temperature adsorption of  $\text{NO} + \text{O}_2$  mixture (16 mbar,  $\text{NO}:\text{O}_2 = 1:1$ ) for 20 min followed by evacuation for 15 min. To the sample treated in this way, 50 mbar of  $\text{CH}_4$  was added and the isolated IR cell was heated in the 423–723 K temperature range with a 50 K ramp for 20 min at each temperature (the so called “ $\text{CH}_4$ - $\text{NO}_x$ ” experiment). The FT-IR spectra are shown in Fig. 5 in which panels a and b display the sample and gas phase spectra, respectively. The room temperature spectrum of the sample (Fig. 5a, spectrum RT) shows the presence of  $\text{Pd}^{2+}$ -NO species at 1884 and  $1820\text{ cm}^{-1}$  [18,19,21] and surface nitrates characterized by the absorption bands at 1648, 1575 and  $1238\text{ cm}^{-1}$  [21,22]. The sharp band marked by an asterisk is due to gaseous methane. The spectra taken at higher temperatures

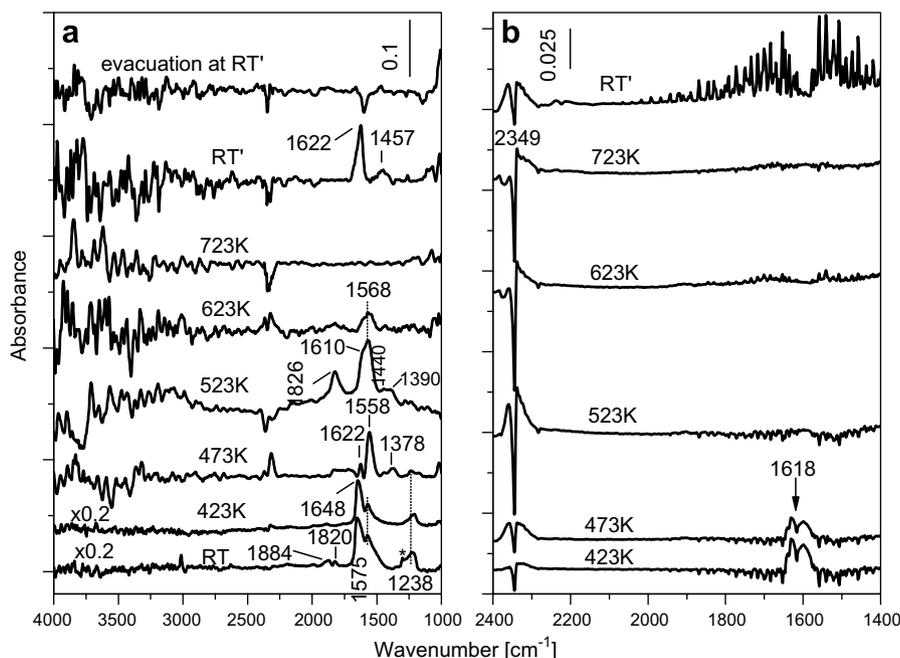


Fig. 5. (a) FT-IR spectrum of the sample  $0.1\text{Pd}/\text{NbZ-P}$  containing adsorbed  $\text{NO}_x$  species (spectrum RT, see the text for the conditions) and spectra taken upon heating in  $\text{CH}_4$  (50 mbar) for 20 min at the indicated temperatures and after cooling to room temperature (spectrum RT') followed by evacuation. (b) Spectra of the gas phase detected at the indicated temperatures.

are gas-phase corrected. The decomposition of the surface nitrates starts at 423 K producing  $\text{NO}_2$  in the gas phase (absorption band at  $1618\text{ cm}^{-1}$  in Fig. 5b). Judging by the extremely low intensity of the band at  $1238\text{ cm}^{-1}$  (Fig. 5a), the heating at 473 K causes an almost complete desorption of the  $\text{NO}_3^-$  species. A new, weak band at  $1378\text{ cm}^{-1}$  appears in the spectrum. The bands at 1648 and  $1575\text{ cm}^{-1}$  shift to  $1622$  and  $1558\text{ cm}^{-1}$ , respectively, and the absorption at  $1622\text{ cm}^{-1}$  has become less intense than that at  $1558\text{ cm}^{-1}$ . In addition, the amount of gaseous  $\text{NO}_2$  at 473 K has decreased relative to that at 423 K (Fig. 5b). This indicates that  $\text{NO}_2$  reacts with the activated methane and as shown in analogous experiment with Pd-promoted tungstated zirconia [22], the product of this interaction is nitromethane. The bands at  $1558$  and  $1378\text{ cm}^{-1}$  are attributed to the  $\nu_{\text{as}}(\text{NO}_2)$  and  $\nu_{\text{s}}(\text{NO}_2)$  modes of adsorbed  $\text{CH}_3\text{NO}_2$ , respectively [22], whereas the absorption at  $1622\text{ cm}^{-1}$  most likely corresponds to residual nitrate species. At 523 K the  $\text{NO}_2$  disappears from the gas phase (Fig. 5b). The sample spectrum at this temperature exhibits bands at  $1826$  and  $1568\text{ cm}^{-1}$  with a shoulder at approximately  $1610\text{ cm}^{-1}$ , and weak absorptions at  $1440$  and  $1390\text{ cm}^{-1}$  (Fig. 5a). Note that the intensities of the bands at  $1610$  and  $1558\text{ cm}^{-1}$  are higher than those of the bands at  $1622$  and  $1558\text{ cm}^{-1}$  observed in the spectrum taken at 473 K. This shows that at 523 K new species are formed as a result of the transformation of nitromethane giving rise to the absorptions at  $1842$ ,  $1615$  and  $1568\text{ cm}^{-1}$ . The former band is characteristic of  $\text{Pd}^+-\text{NO}$  nitrosyls [21,22] and the bands at  $1568$  and  $1390\text{ cm}^{-1}$  are attributed to the  $\nu_{\text{as}}(\text{CO}_2)$  and  $\nu_{\text{s}}(\text{CO}_2)$  modes of formate species, respectively, [21,22]. The absorptions at  $1610$  ( $\nu(\text{N}=\text{O})$ ) and  $1440\text{ cm}^{-1}$  ( $\delta(\text{CH}_3)$ ) most likely belong to *cis*-methyl nitrite,  $\text{CH}_3\text{ONO}$  [22]. As proposed earlier [22] the decomposition of nitromethane on Pd-promoted tungstated zirconia takes place through the intermediacy of *cis*- $\text{CH}_3\text{ONO}$  leading to the formation of adsorbed NO and formate species. Apparently, the surface  $\text{CH}_4-\text{NO}_x$  reaction on the 0.1Pd/NbZ-P sample follows the same mechanistic scheme proposed for Pd-promoted tungstated zirconia [22]. Increasing the temperature to 623 K causes an almost complete vanishing of the adsorbed NO and a strong decrease in the intensities of the formate bands as a result of the  $\text{NO} + \text{HCOO}^-$  interaction to  $\text{N}_2$  [22]. The spectrum taken after cooling to room temperature (spectrum RT') contains bands at  $1622$  and  $1457\text{ cm}^{-1}$  assigned to  $\text{CO}_3^{2-}$  and/or  $\text{HCO}_3^-$  species [22]. In contrast to the surface nitrates, the carbonate species are weakly adsorbed and leave the surface during the evacuation at room temperature.

The investigation of the thermal stability of the  $\text{NO}_x$  species adsorbed on the 0.1Pd/NbZ-P sample (the so called "Blank  $\text{NO}_x$ " experiment) shows that in the absence of methane,  $\text{NO}_2$  is present in the gas phase over the sample up to 723 K. The spectrum, taken after cooling to room temperature, contains bands at  $1870$  and  $1820\text{ cm}^{-1}$  corresponding to  $\text{Pd}^{2+}-\text{NO}$  species and absorptions at  $1635$ ,

$1575$  and  $1232\text{ cm}^{-1}$  due to surface nitrates. The reappearance of adsorbed  $\text{NO}_x$  species in  $\text{CH}_4$ -free atmosphere supports the conclusion that the 0.1Pd/NbZ-P sample catalyzes the reduction of  $\text{NO}_x$  to  $\text{N}_2$  in the presence of the hydrocarbon. The formation of intermediates during the  $\text{CH}_4-\text{NO}_x$  surface reaction on the 0.1Pd/NbZ-P catalyst, such as oxygenate species (formate ions) and adsorbed NO, is in agreement with the results of recent mechanistic studies on catalysts proven to be active in the reduction of NO with methane in excess oxygen [24,25].

The surface nitrates on the Pd-free NbZ-P sample decompose also to  $\text{NO}_2$ . However, there is no evidence of the formation of intermediates such as nitromethane, formate species and adsorbed NO, indicating that this material is inactive in the  $\text{CH}_4-\text{NO}_x$  surface reaction.

Finally, the fact that the surface  $\text{HCO}_3^-/\text{CO}_3^{2-}$  species (formed in the " $\text{CH}_4-\text{NO}_x$ " experiment) are weakly adsorbed (see Fig. 5a, spectra RT' and evacuation at RT') suggests that  $\text{Zr}_6\text{Nb}_2\text{O}_{17}$  has low surface basicity. This result points to the possibility of the application of Pd-promoted  $\text{Zr}_6\text{Nb}_2\text{O}_{17}$  as  $\text{CH}_4$ -SCR catalyst which could be resistant to  $\text{SO}_2$  poisoning. For example, Ziolek et al. [23] concluded that the resistance of Cu-ZSM-5 catalysts to sulfation is improved if niobium is incorporated in the lattice. Forthcoming experiments involving adsorption of  $\text{SO}_2$  will test the potential of this material for the development of  $\text{SO}_2$ -tolerant palladium catalysts for the reduction of NO with methane in the presence of oxygen.

#### 4. Conclusions

The impregnation of hydrated zirconia ( $\text{ZrO}_x(\text{OH})_{4-2x}$ ) with the peroxoniobium(V) complex,  $[\text{Nb}_2(\text{O}_2)_3]^{4+}$ , ensuring  $\text{ZrO}_2:\text{Nb}_2\text{O}_5$  mole ratio of 6:1 followed by calcination at 873 K leads to the formation of  $\text{Zr}_6\text{Nb}_2\text{O}_{17}$ . In contrast, the application of Nb(V) oxalate precursor (keeping the  $\text{ZrO}_2:\text{Nb}_2\text{O}_5$  mole ratio the same) results in an  $\text{Nb}_2\text{O}_5-\text{ZrO}_2$  sample that contains a phase of  $\text{Nb}_2\text{O}_5$ . The formation of  $\text{Zr}_6\text{Nb}_2\text{O}_{17}$  is favored by the partial solubility of hydrous zirconia in the  $\text{H}_2\text{O}_2$  solution. This compound possesses a sufficient amount of strong Brønsted acid sites allowing a good dispersion of deposited Pd(II) species. Pd-promoted  $\text{Zr}_6\text{Nb}_2\text{O}_{17}$  is a novel solid acid that has the potential of a catalyst for the selective reduction of NO with methane in the presence of oxygen.

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