



# NO selective reduction by hydrogen on potassium titanate supported palladium catalyst

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## ABSTRACT

Potassium titanate (K<sub>2</sub>O–6TiO<sub>2</sub>) nanowires were successfully prepared by alkali treatment of TiO<sub>2</sub> (79% anatase, 21% rutile) under autogenous pressure in a Teflon-lined autoclave at 200 °C. After further modification with 1 wt.% Pd by wet impregnation, the calcined and pre-reduced Pd/K<sub>2</sub>O–6TiO<sub>2</sub> catalyst was applied for selective reduction of NO<sub>x</sub> by H<sub>2</sub> (H<sub>2</sub>–SCR) under lean conditions, together with Pd/Al<sub>2</sub>O<sub>3</sub> and Pd/TiO<sub>2</sub> as reference. The reference catalysts exhibited maximum NO conversion of about 50–60% at 100–130 °C, but with low N<sub>2</sub> selectivity. The N<sub>2</sub> selectivity on Pd/K<sub>2</sub>O–6TiO<sub>2</sub> was considerably high, reaching 80% at maximum, with only 11% conversion of the admixed hydrogen reductant. In situ DRIFT spectroscopy revealed surface-fixed nitrates and Pd-bound NO, but no NH<sub>x</sub> ad-species. It is concluded, that the beneficial effect of the K<sub>2</sub>O–6TiO<sub>2</sub> support is due mainly to a stabilization of high Pd dispersion with enhanced concentration of Pd<sup>0</sup>–NO intermediates, and due to support alkalinity, that enhances nitrate fixation.

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## 1. Introduction

Nitrogen oxides, from stationary and transportation sources, are major air pollutants that greatly contribute to the formation of photochemical smog and acid rain [1]. Various post-treatment methods have been attempted for the reduction of NO<sub>x</sub> emissions. In the case of stationary sources, the selective catalytic reduction of NO<sub>x</sub> by ammonia (NH<sub>3</sub>–SCR), a state-of-the-art technology for NO<sub>x</sub> abatement, has been extensively studied. The vanadia/titania-based catalysts have already been commercially used in the industrial scale. However, under road conditions, the risk of vanadia emissions and NH<sub>3</sub> slip causes safety concerns [2]. Because ammonia synthesis needs hydrogen, it is desirable to use hydrogen directly as NO<sub>x</sub> reductant, without intermediate processing to ammonia. Therefore, the selective catalytic reduction of NO<sub>x</sub> by hydrogen (H<sub>2</sub>–SCR), is regarded as good alternative for NH<sub>3</sub>–SCR and is receiving increasing attention.

Supported platinum catalysts are initially found to be active for the H<sub>2</sub>–SCR reaction at low temperatures in 1997 [3]. Subsequently, Pt/SiO<sub>2</sub> [4,5], Pt/TiO<sub>2</sub>–ZrO<sub>2</sub> [6], Pt/La<sub>0.5</sub>Ce<sub>0.5</sub>MnO<sub>3</sub> [7], Pt/MFI [8,9] and Pt/Mg–Al–O [10] have been reported to be promising catalysts for H<sub>2</sub>–SCR reaction. More recently, supported palladium catalysts, such as Pd/TiO<sub>2</sub> [11], Pd/Al<sub>2</sub>O<sub>3</sub> [12], Pd/V<sub>2</sub>O<sub>5</sub>/Al<sub>2</sub>O<sub>3</sub> [13]

and Pd/TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> [14] are also reported to be highly active in H<sub>2</sub>–SCR reaction. However, the activity of supported platinum and palladium catalysts for NO reduction is usually achieved at the expense of a high hydrogen consumption (usually ~100%), that means, most of the hydrogen reacts with excess oxygen in the reaction system directly to water. Moreover, the formation of the undesired byproduct N<sub>2</sub>O is a serious problem to be solved.

In this work, potassium titanate supported palladium (Pd/K<sub>2</sub>O–6TiO<sub>2</sub>) is described as a promising alternative catalyst formulation for the H<sub>2</sub>–SCR reaction, with good catalytic performance at a comparatively low hydrogen consumption. The catalyst exhibits good activity and N<sub>2</sub> selectivity, as compared with Pd/TiO<sub>2</sub> and Pd/Al<sub>2</sub>O<sub>3</sub>. A detailed structural and textural characterization was performed using XRD, Raman spectroscopy, TEM, N<sub>2</sub> adsorption, and TPR. The Pd dispersion was determined by H<sub>2</sub> titration. Surface species and intermediates of NO<sub>x</sub> conversion were studied by means of in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). Key points of the reaction mechanism will be discussed.

## 2. Experimental

### 2.1. Catalyst preparation

Potassium titanate with nanorod morphology was prepared from TiO<sub>2</sub> (Degussa P25, anatase 79%, rutile 21%) by an alkali treatment, as described in reference [15,16]. In a typical synthesis, 10 g

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TiO<sub>2</sub> powder and 100 mL KOH solution (10 M) were mixed together. After vigorous stirring for about 2 h, the mixture was transferred into a Teflon-lined autoclave (125 mL) and heated at 200 °C for 48 h. The precipitate was filtrated and thoroughly washed with distilled water until pH < 9. Then, the precipitate was dried at 80 °C overnight and calcined at 400 °C in flowing air for 4 h.

The as-synthesized potassium titanate, together with TiO<sub>2</sub> (Degussa P25) and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (Tosoh Co.), was used as catalyst support. Palladium was introduced into the supports by wet impregnation with an aqueous palladium(II) chloride solution sufficient to yield 1% Pd loading. After impregnation, the catalysts were again dried overnight and calcined at 400 °C in flowing air for 4 h.

## 2.2. Catalyst characterization

Powder X-ray diffraction (XRD) measurements were carried out on the samples using a Rigaku D/max 2500 diffractometer, equipped with a graphite monochromator and using Cu K $\alpha$  radiation. Raman spectroscopy was carried out with a Renishaw InVia Raman Spectrometer. Spectra were obtained with the green line of an Ar-ion laser (514.53 nm) in micro-Raman configuration.

Transmission electron microscopy (TEM) images of samples were acquired on a Tecnai G<sup>2</sup> 20 S-TWIN transmission electron microscope at an accelerate voltage of 200 kV.

The textural properties of catalysts were analyzed by low-temperature N<sub>2</sub> adsorption/desorption using a Quantachrome NOVA-1200 gas absorption analyzer and the specific surface areas were calculated using the BET equation.

H<sub>2</sub>-TPR was carried out in a microreactor using 50 mg of sample for each run. The sample was pretreated in flowing air at 400 °C for 2 h and then cooled down to 50 °C in flowing He. At constant temperature of 50 °C, the flow of H<sub>2</sub>/He (5% H<sub>2</sub>, 30 mL min<sup>-1</sup>) was switched to the sample, and after 30 min the temperature-programmed reduction was started from 50 °C to 250 °C with a temperature ramp of 5 °C min<sup>-1</sup>. The consumption of the reducing agent H<sub>2</sub> was measured on-line by a gas chromatograph equipped with a TCD.

## 2.3. Catalytic testing

The selective catalytic reduction of NO by hydrogen was performed in a fixed-bed flow microreactor at atmospheric pressure. Typically, 0.1 g of sample (sieve fraction, 0.25–0.5 mm) was placed in a quartz reactor (4 mm i.d.) and pretreated in H<sub>2</sub>/He (0.1% H<sub>2</sub>) at 400 °C for 1 h. After cooling to 50 °C in He, the reactant gas mixture (1000 ppm NO, 5000 ppm H<sub>2</sub>, 5% O<sub>2</sub>, He balance) was fed to the reactor. The total flow rate of the gas mixture was 100 mL min<sup>-1</sup>, corresponding to a GHSV of 60,000 h<sup>-1</sup>. The steady-state tests were conducted isothermally every 25 °C from 50 °C to 300 °C. The reactant and product gas composition was analyzed on-line using a gas chromatograph (HP 6890 series) equipped with a TCD. A HP-PLOT MoleSieve column served for separation of H<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, and a Poraplot Q column for the separation of N<sub>2</sub>O and NO. Simultaneously, the exit stream composition was continuously analyzed by a multi-gas sensor Mulptor 610 (Maihak, Germany) equipped with a non-dispersive infrared channel for NO, and a NO<sub>2</sub>-NO converter reducing NO<sub>2</sub> to NO over a molybdenum catalyst. The difference between NO/NO<sub>2</sub> and NO concentration gives the NO<sub>2</sub> content. The nitrogen balance was calculated using the following equation:  $[\text{NO}]_{\text{inlet}} = [\text{NO}]_{\text{outlet}} + 2[\text{N}_2\text{O}]_{\text{outlet}} + 2[\text{N}_2]_{\text{outlet}} + [\text{NO}_2]_{\text{outlet}}$ . This N-balance was found to be >95% for all experiments. The NO conversion is calculated as  $X_{\text{NO}} = ([\text{NO}]_{\text{inlet}} - [\text{NO}]_{\text{outlet}})/[\text{NO}]_{\text{inlet}}$  and the H<sub>2</sub> conversion as  $X_{\text{H}_2} = ([\text{H}_2]_{\text{inlet}} - [\text{H}_2]_{\text{outlet}})/[\text{H}_2]_{\text{inlet}}$ . The N<sub>2</sub> selectivity is calculated as  $S_{\text{N}_2} = 2 * [\text{N}_2]/([\text{NO}]_{\text{inlet}} - [\text{NO}]_{\text{outlet}})$ , while the N<sub>2</sub>O and NO<sub>2</sub> selectivity is calculated as  $S_{\text{N}_2\text{O}} = 2 * [\text{N}_2\text{O}]/$

$([\text{NO}]_{\text{inlet}} - [\text{NO}]_{\text{outlet}})$  and  $S_{\text{NO}_2} = [\text{NO}_2]/([\text{NO}]_{\text{inlet}} - [\text{NO}]_{\text{outlet}})$ , respectively. The N<sub>2</sub> yield is calculated as  $Y_{\text{NO}} = 2 * [\text{N}_2]/[\text{NO}]_{\text{inlet}}$ .

## 2.4. DRIFT studies

DRIFT studies were performed on the spectrometer FTS-60A (BIO-RAD) by using a diffuse reflectance attachment (HARRICK) equipped with a reaction chamber. A number of 256 single beam spectra had been co-added at a resolution of 4 cm<sup>-1</sup> and the spectra were presented as absorbance function referred to adequate background spectra. For the in situ DRIFT measurements all catalysts were used as powders (about 75 mg). Prior to the reduction of NO all catalysts were pretreated in the following way: heating in H<sub>2</sub>/He (0.1% H<sub>2</sub>) at a rate of 10 °C min<sup>-1</sup> up to 400 °C and holding at 400 °C for 1 h, then cooling down to 80 °C. Subsequently, NO reduction was started under the following feed mixtures: NO (2000 ppm), H<sub>2</sub> (1%), O<sub>2</sub> (10%) (balance He) using a total flow of 40 mL min<sup>-1</sup> at 80 °C. After holding this temperature for 20 min, it was stepwise increased to the next temperature at the heating rate of 10 °C min<sup>-1</sup>. The DRIFT spectra were recorded every 25 °C (from 80 to 255 °C) after 20 min of steady-state reaction.

## 3. Results and discussion

### 3.1. Catalyst characterization

The XRD pattern of as-synthesized sample K<sub>2</sub>O-6TiO<sub>2</sub> is shown in Fig. 1, where all diffraction lines are in good agreement with those of standard pattern for monoclinic K<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub> (space group: C2/m; lattice constants:  $a = 1.5593$  nm,  $b = 0.3796$  nm,  $c = 0.9108$  nm; JCPDS # 40-0403). The structure of the sample is further characterized by Raman spectroscopy, as shown in Fig. 2. Raman bands at 280, 390, 450, 650 and 860 cm<sup>-1</sup> can be observed, which agree with the characteristic bands of K<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub> [17]. The band at 900 cm<sup>-1</sup> is attributed to the four coordinated Ti-O stretching modes that stuck out into the interlayer spaces [18]. Notably, the as-synthesized K<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub> is also recognized as K<sub>2</sub>O-6TiO<sub>2</sub>, a type of compounds with potassium inserting the layer of TiO<sub>2</sub> [19].

The TEM image of as-synthesized potassium titanate in Fig. 3 shows the structure of nanorods with narrow size distribution. The uniform diameters are about 10 nm, and the lengths amount to more than 100 nm. The morphology of nanorods is well preserved after Pd impregnation and calcination as shown in Fig. 4. Moreover, no bulk Pd can be observed, owing to the good

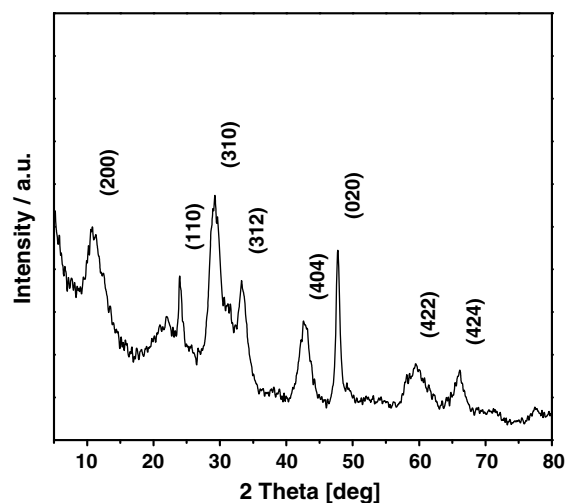


Fig. 1. XRD patterns of as-synthesized potassium titanate.

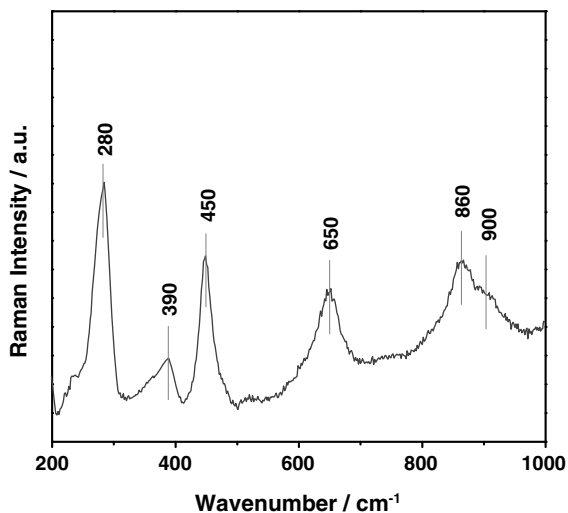


Fig. 2. Raman spectra of as-synthesized potassium titanate.

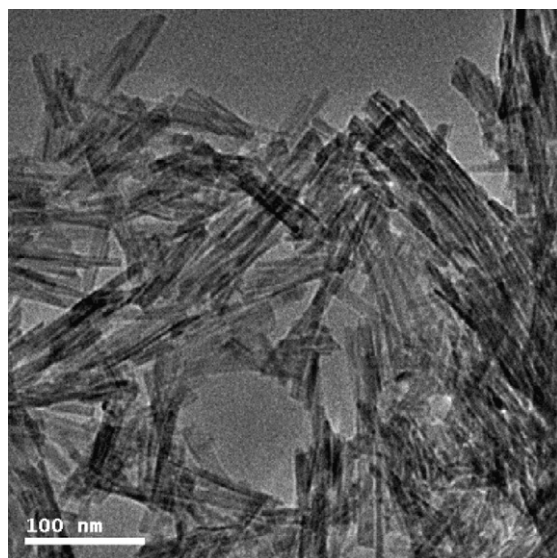


Fig. 3. TEM image of as-synthesized potassium titanate.

dispersion of Pd species (83%) as determined by H<sub>2</sub> chemisorption (Table 1). Some textural properties of Pd/K<sub>2</sub>O–6TiO<sub>2</sub>, Pd/TiO<sub>2</sub> and Pd/Al<sub>2</sub>O<sub>3</sub> are summarized in Table 1.

The H<sub>2</sub>-TPR profiles of Pd/K<sub>2</sub>O–6TiO<sub>2</sub>, Pd/TiO<sub>2</sub>, and Pd/Al<sub>2</sub>O<sub>3</sub> are shown in Fig. 5. The main reduction of Pd on TiO<sub>2</sub> takes places at temperatures lower than 50 °C, so that no distinct reduction peak could be recorded. In the case of Pd/Al<sub>2</sub>O<sub>3</sub> and Pd/K<sub>2</sub>O–6TiO<sub>2</sub>, reduction peaks are observed at 130 °C and 160 °C, respectively. From the comparison between Pd/TiO<sub>2</sub> and Pd/K<sub>2</sub>O–6TiO<sub>2</sub>, it is believed that the addition of K<sub>2</sub>O significantly retards the reduction of Pd<sup>2+</sup>, similar to the results reported by Qi et al. [14] and Zhu et al. [20].

### 3.2. H<sub>2</sub>-SCR of NO<sub>x</sub>

The performance of Pd/TiO<sub>2</sub>, Pd/Al<sub>2</sub>O<sub>3</sub> and Pd/K<sub>2</sub>O–6TiO<sub>2</sub> catalysts is shown in Fig. 6. The highest NO conversion can be observed on Pd/TiO<sub>2</sub> (60%, at 104 °C), followed by Pd/Al<sub>2</sub>O<sub>3</sub> (53%, at 128 °C) and Pd/K<sub>2</sub>O–6TiO<sub>2</sub> (41%, at 164 °C), as shown in Fig. 6a. Whereas the H<sub>2</sub> conversion reaches 100% on Pd/TiO<sub>2</sub> and Pd/Al<sub>2</sub>O<sub>3</sub> at the

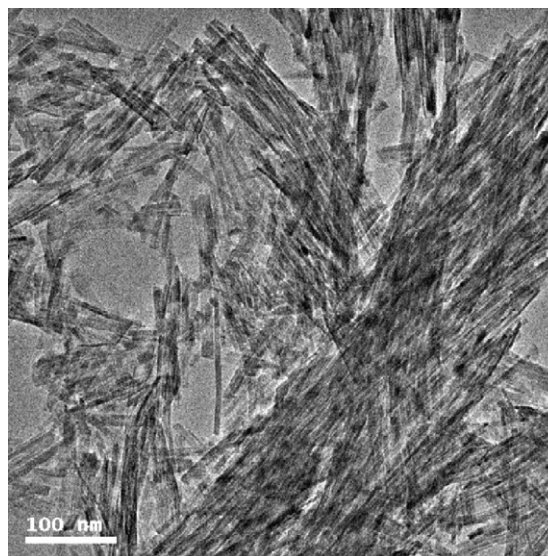


Fig. 4. TEM image of potassium titanate supported palladium catalyst.

**Table 1**  
Textural properties of Pd-based catalysts

Catalyst <sup>a</sup>	Surface area (m <sup>2</sup> g <sup>-1</sup> )	Pd loading (%) <sup>b</sup>	Pd dispersion (%) <sup>c</sup>
Pd/TiO <sub>2</sub>	25.7	0.94	59
Pd/Al <sub>2</sub> O <sub>3</sub>	221.8	0.95	66
Pd/K <sub>2</sub> O–6TiO <sub>2</sub>	182.6	0.92	83

<sup>a</sup> Treated in H<sub>2</sub>/He for 1 h at 400 °C.

<sup>b</sup> By weight.

<sup>c</sup> Determined by H<sub>2</sub> chemisorption and dispersion is calculated as [H uptake]/[Pd loading].

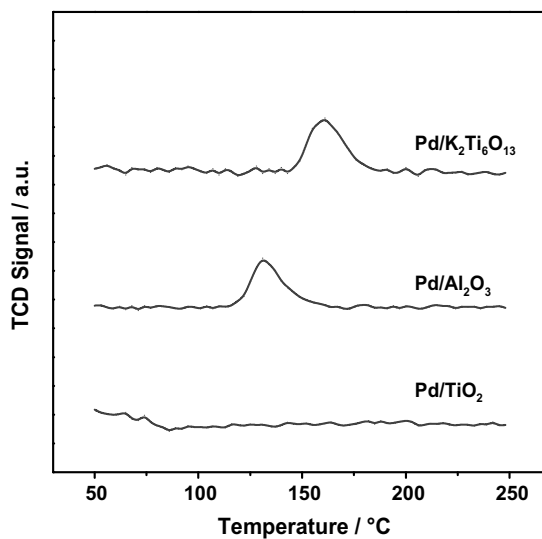


Fig. 5. H<sub>2</sub>-TPR profiles of supported palladium catalysts.

temperature where the maximal NO conversion is achieved (Fig. 6b), only 11% of admixed H<sub>2</sub> is converted on Pd/K<sub>2</sub>O–6TiO<sub>2</sub> at the temperature of maximal NO conversion. Obviously, the undesired reaction between H<sub>2</sub> and O<sub>2</sub> (H<sub>2</sub> + O<sub>2</sub> → H<sub>2</sub>O) is greatly retarded on Pd/K<sub>2</sub>O–6TiO<sub>2</sub>. This means, H<sub>2</sub> acts more selective for the reduction of NO on Pd/K<sub>2</sub>O–6TiO<sub>2</sub>. The N<sub>2</sub> selectivity on the catalysts varies with reaction temperature, as shown in Fig. 6c, but is significantly higher on Pd/K<sub>2</sub>O–6TiO<sub>2</sub> than on Pd/TiO<sub>2</sub> and Pd/

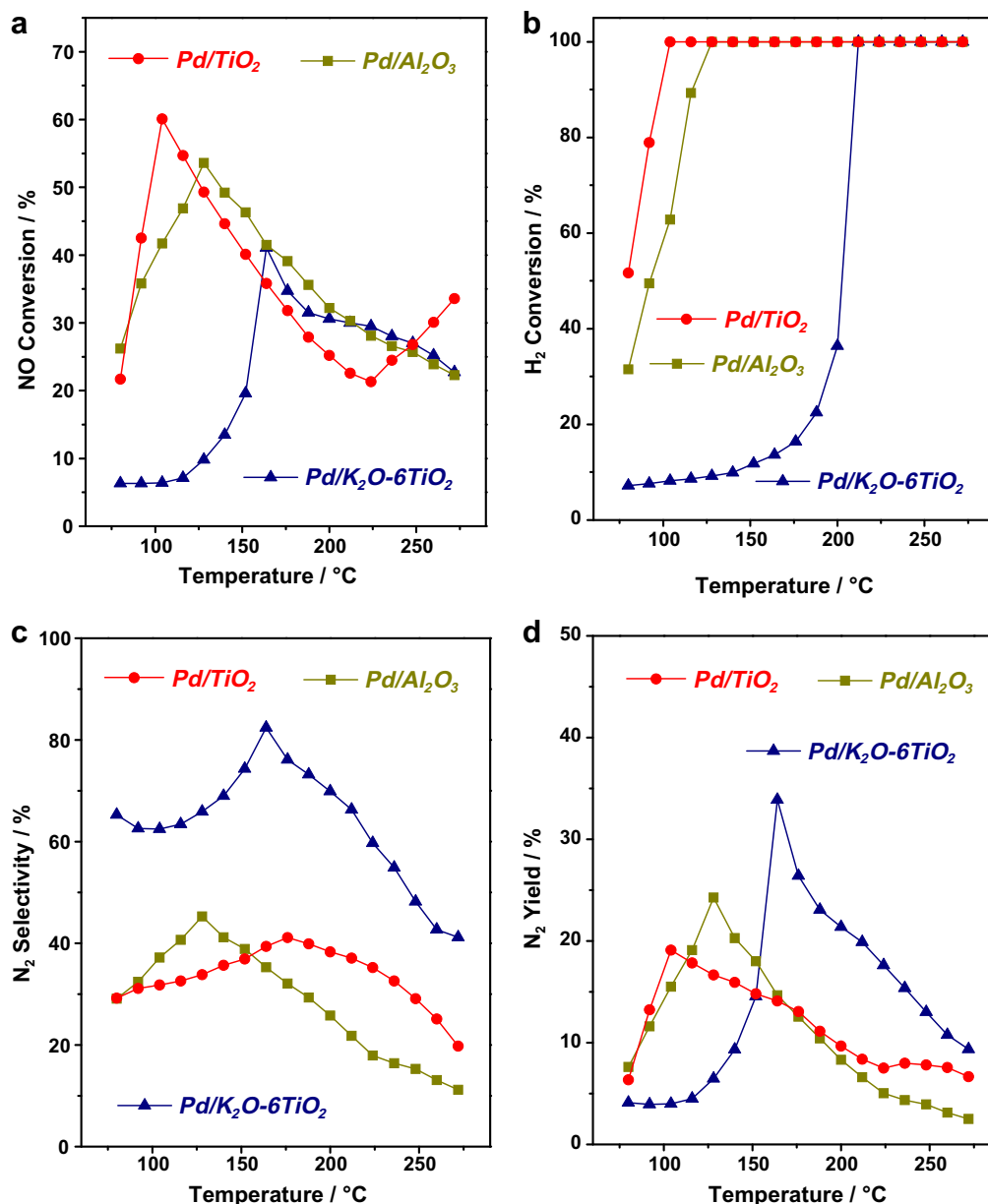


Fig. 6. Catalytic performance of supported palladium catalysts for NO–H<sub>2</sub>–O<sub>2</sub> reaction. Reaction conditions: NO = 1000 ppm, H<sub>2</sub> = 5000 ppm, O<sub>2</sub> = 5%, He balance; GHSV = 60,000 h<sup>-1</sup>.

Al<sub>2</sub>O<sub>3</sub>. Finally, the N<sub>2</sub> yield over Pd/K<sub>2</sub>O–6TiO<sub>2</sub> is superior to the reference catalysts at the temperature window 160–260 °C.

The activity of the support (not shown) is lower than 10% NO conversion up to reaction temperatures of 200 °C, with moderate H<sub>2</sub> oxidation between 80 and 164 °C (15% at maximum). However, it must be stated, that the support material is capable to catalyze the deNO<sub>x</sub> reaction at temperatures higher than 200 °C with maximum NO conversion of nearly 20% and about 50% N<sub>2</sub> selectivity at 275 °C, under complete H<sub>2</sub> consumption. These reactivity characteristics are comparable to the performance of the Pd/K<sub>2</sub>O–6TiO<sub>2</sub> catalyst at temperatures beyond 200 °C. Therefore, the reaction at temperatures higher than 200 °C benefits from the influence of the support.

A detailed analysis of the product selectivity profile of Pd/K<sub>2</sub>O–6TiO<sub>2</sub> is displayed in Fig. 7. N<sub>2</sub>O and NO<sub>2</sub> are observed as products, besides N<sub>2</sub>. It is striking that the N<sub>2</sub> and N<sub>2</sub>O selectivity exhibit a mirror-like dependence on the reaction temperature with a sharp

inversion point at 160–165 °C. These profiles indicate that both products are competitively formed from the same intermediate. Anticipating results of DRIFT spectroscopy (see Section 3.3) the most abundant intermediates are surface-fixed nitrates.

### 3.3. DRIFT studies

DRIFT spectra obtained under reaction conditions over Pd/K<sub>2</sub>O–6TiO<sub>2</sub> at different temperatures are shown in Fig. 8. At 80 °C, strong bands at 1605, 1585 and 1370 cm<sup>-1</sup> as well as some weak bands at 1750, 1300 and 1260 cm<sup>-1</sup> have been observed. The bands at 1605 and 1260 cm<sup>-1</sup> are assigned to bridging nitrate species on the K<sub>2</sub>O–6TiO<sub>2</sub> support, while the bands at 1585 and 1300 cm<sup>-1</sup> are assigned to chelating nitrate species on the K<sub>2</sub>O–6TiO<sub>2</sub> support [21,22]. The multi-bands centered at 1370 cm<sup>-1</sup> (1340–1400 cm<sup>-1</sup>) are assigned to water-solvated nitrate species, as suggested by Goodman et al. [23]. The weak band at 1750 cm<sup>-1</sup> may be as-

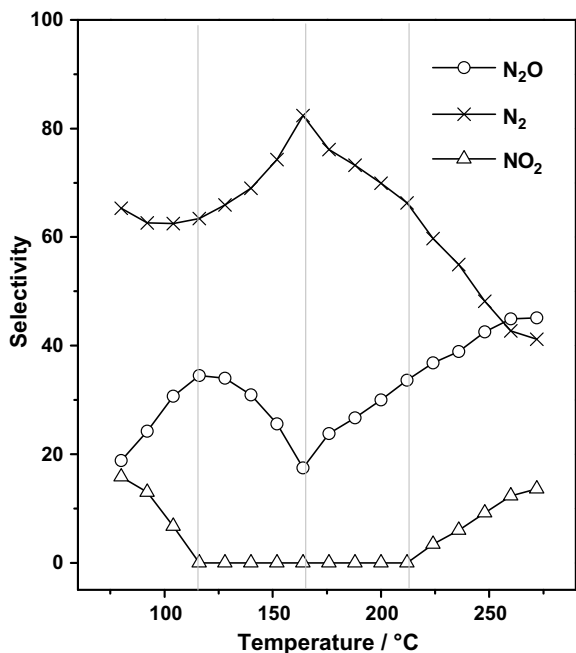


Fig. 7. Product selectivity for NO-H<sub>2</sub>-O<sub>2</sub> reaction over Pd/K<sub>2</sub>O-6TiO<sub>2</sub> catalyst.

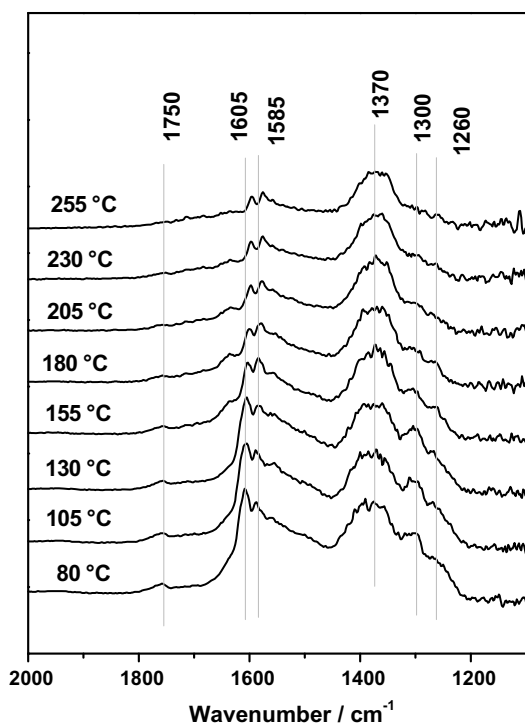


Fig. 8. DRIFTS study of adsorbed species formed on surface of Pd/K<sub>2</sub>O-6TiO<sub>2</sub> catalyst under NO-H<sub>2</sub>-O<sub>2</sub> reaction condition: 2000 ppm NO + 1% H<sub>2</sub> + 10% O<sub>2</sub> with He balance.

signed to linear Pd<sup>0</sup>-NO species [11,14], i.e., gaseous NO adsorbs on the surface of Pd, with no band dissociation [24].

With increasing temperatures, the intensity of the IR band associated with linear Pd<sup>0</sup>-NO species decreased gradually and, eventually, disappeared at 180 °C. The intensities of IR bands associated with various coordinated nitrates on the K<sub>2</sub>O-6TiO<sub>2</sub> support increased first to a maximum (at 155 °C) and then began to decrease with increasing temperatures. The IR bands corresponding

to water-solvated nitrate species remained unchanged over the whole temperature range.

### 3.4. Mechanism consideration

It is known that fixation of NO in the presence of excess O<sub>2</sub> on noble metals as well as support oxides occurs in form of surface nitrates which are reactive towards H<sub>2</sub> [6]. By dissociation of H<sub>2</sub>, the noble metal supplies H which reacts with nitrates species located on the support. Reduction of the surface species should (desirably) stop at the stage of N<sub>2</sub>, but can also lead to NH<sub>3</sub> [12], according to the catalyst system, feed composition and reaction conditions. DRIFT spectroscopic studies of the NO-H<sub>2</sub>-O<sub>2</sub> reaction on Pd/Al<sub>2</sub>O<sub>3</sub> and Pd/TiO<sub>2</sub> catalysts revealed adsorbed NH<sub>x</sub> species as intermediates that enable an in situ NH<sub>3</sub>-SCR reaction route [11,12]. These species could not be observed during N<sub>2</sub>-SCR on the present catalysts, probably, owing to the redox properties of the feed (O<sub>2</sub>/H<sub>2</sub> = 10).

For comparing the catalytic and DRIFT results, it should be noted that the present findings relate to the catalyst used after pre-reduction with H<sub>2</sub> at 400 °C. After pre-reduction at 400 °C, Pd<sup>2+</sup> is converted to Pd<sup>0</sup> (vide TPR). Nevertheless, the palladium dispersion is kept as high as 83% (Table 1), i.e., palladium is present in a nearly atomic dispersion. Therefore, no Pd clusters are detectable by TEM (Fig. 4). Interaction of Pd<sup>0</sup> with NO leads to Pd<sup>0</sup>-NO species as revealed by DRIFTS (Fig. 8). Simultaneously, gaseous NO reacts with O<sub>2</sub> to NO<sub>2</sub> and, consecutively, to surface nitrates, which could preferentially be fixed to basic sites (K<sub>2</sub>O) of the support, similar to the NO<sub>x</sub> storage process [25].

Whereas for Pd/Al<sub>2</sub>O<sub>3</sub> and Pd/TiO<sub>2</sub> the complete consumption of H<sub>2</sub> coincides with the maximum of NO conversion as known from literature data [12], the consumption of H<sub>2</sub> is only about 11% at maximum NO conversion for sample Pd/K<sub>2</sub>O-6TiO<sub>2</sub>.

Importantly, the Pd/K<sub>2</sub>O-6TiO<sub>2</sub> catalyst contains zero-valent Pd after pre-reduction at 400 °C. Since the activation energy for oxygen dissociation is higher for Pd than for PdO [26], it is concluded that the low percentage of H<sub>2</sub> oxidation within the activity range between 80 and 164 °C is caused by poor oxygen activation. Presumably, NO<sub>2</sub> (and surface nitrates) are formed from Pd<sup>0</sup>-NO and gaseous O<sub>2</sub>. With temperature increase, the concentration of Pd<sup>0</sup>-NO decreases and Pd<sup>0</sup> is oxidized. Indeed, after reaction at 275 °C, the catalyst contains Pd<sup>2+</sup> as revealed by XPS measurements (not shown). The reaction temperature of 164 °C seems to indicate a modification of the mechanism. Whereas a low-temperature route is characterized by H-assisted dissociation of NO dominating on Pd<sup>0</sup> sites, a high-temperature route is accomplished by H-assisted reduction of nitrates on the support. NO<sub>2</sub> and N<sub>2</sub>O is produced by thermal decomposition of surface nitrates [27], with deterioration of N<sub>2</sub> selectivity. Further investigations are necessary to clarify details of the mechanism of the complex catalyst system.

## 4. Conclusion

The Pd/K<sub>2</sub>O-6TiO<sub>2</sub> catalyst exhibits good deNO<sub>x</sub> behavior in the NO-H<sub>2</sub>-O<sub>2</sub> reaction under lean conditions, where maximum conversion of NO can be achieved at comparatively low consumption of the H<sub>2</sub> reductant. Characterization data and in situ DRIFT spectroscopy revealed that Pd<sup>0</sup> is stabilized in high dispersion, and actually, the activation of gas phase oxygen is limited in the low-temperature activity range (80–164 °C). The support-induced modification of Pd<sup>0</sup> limits the H<sub>2</sub> consumption but, nevertheless, enables the H-assisted NO dissociation via Pd<sup>0</sup>-NO intermediates. The temperature window of optimum performance is small. At higher reaction temperatures NO<sub>2</sub> and N<sub>2</sub>O are produced by thermal decomposition of surface nitrates, with deterioration of N<sub>2</sub> selectivity. At this range the support starts to become active as well.

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