

# Mechanism of Nitrite Hydrogenation based on ATR-IR Spectroscopy

Koteswara Rao Nidadavolu<sup>1</sup>, Barbara L. Mojet<sup>1</sup>, Leon Lefferts<sup>1\*</sup>

<sup>1</sup>Catalytic process and materials group, Faculty of Science and Technology,  
University of Twente, Enschede, The Netherlands

\*corresponding author: l.lefferts@utwente.nl

## Introduction

Increasing nitrite and nitrate levels in ground water cause environmental concerns and increasingly strict water quality regulations require removal of nitrite and nitrate from ground water. The most promising method for nitrate and nitrite removal is based on selective hydrogenation over noble metal catalysts [1]. The exact identification of the adsorbates is crucial for a comprehensive understanding of the nitrite hydrogenation mechanism and the connection between surface intermediates and macroscopic selectivity towards nitrogen (desired) or ammonia. This paper discusses the mechanism of nitrite hydrogenation based on ATR-IR spectroscopy, supported by isotopic labeling of nitrite [2].

## Experimental

Pd (5wt %) / $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was prepared by impregnation method. The catalyst was calcined at 300° in air and reduced in H<sub>2</sub> for 3h. about 5mg was spray coated on ZnSe crystal. All catalysts on ZnSe were in-situ reduced before nitrite adsorption/hydrogenation. The nitrites were adsorbed on hydrogen covered palladium and the resulting adsorbed species were hydrogenated using H<sub>2</sub>/H<sub>2</sub>O. The adsorbed species and intermediates during this sequence were studied using ATR-IR.

## Results and Discussion

Fig. 1a shows the ATR-IR spectrum of H-Pd/Al<sub>2</sub>O<sub>3</sub> exposed to <sup>14</sup>N<sup>16</sup>O<sub>2</sub><sup>-</sup> solution. Bands at 1237, 1321, 1350, 1402 cm<sup>-1</sup> originate from nitrite anion [3-4]. The bands at 1350 and 1400cm<sup>-1</sup> were not observed when pure alumina or ZnSe were exposed to nitrite solution. These bands are observed with Pd/Al<sub>2</sub>O<sub>3</sub>. In addition to these peaks, additional peaks are observed at 1510, 1580, 1637, 1720cm<sup>-1</sup>. These peaks show that part of the nitrite ions are initially hydrogenated on H-Pd/Al<sub>2</sub>O<sub>3</sub> on exposure to nitrite solution and intermediates during hydrogenation are adsorbed on the surface. NO, NO<sub>x</sub>H<sub>y</sub>, NH<sub>2</sub> are possible intermediates during hydrogenation of nitrite ion. The peak at 1720 cm<sup>-1</sup> corresponds to NO [5]. we previously assigned the peak at 1510 cm<sup>-1</sup> to NH<sub>2(ads)</sub> [3]. The fact that the position of the peak observed at 1510cm<sup>-1</sup> with <sup>14</sup>N<sup>16</sup>O<sub>2</sub><sup>-</sup> shifts when <sup>15</sup>N<sup>16</sup>O<sub>2</sub><sup>-</sup> is used, as well as when exposed to <sup>15</sup>N<sup>18</sup>O<sub>2</sub><sup>-</sup>. It shows that the previous assignment of 1510cm<sup>-1</sup> doesn't corresponds to NH<sub>2(ads)</sub>. The Peak shift with isotopic labeling shows that the surface species apparently contain both N as well as O and therefore we tentatively assign the peak to NO<sub>x</sub>H<sub>y(ads)</sub>. The band at 1720cm<sup>-1</sup> was assigned to the NO adsorption on Pd surface. It is also conforms with isotopic labeling. The peak at 1580cm<sup>-1</sup> was assigned to NO bridged adsorption over Pd. unexpected isotopic shift was observed when studied with nitrite isotopes. We don't have any explanation at this moment for this unexpected isotopic shift. We observed difference in the ratio's of these three peaks both with labeled and unlabelled Nitrite. It indicates difference in rates of the elementary steps during titration of H<sub>a</sub> by NO<sub>2</sub><sup>-</sup> and also determines the concentration of adsorbed species that are trapped by exhaustion of adsorbed hydrogen.

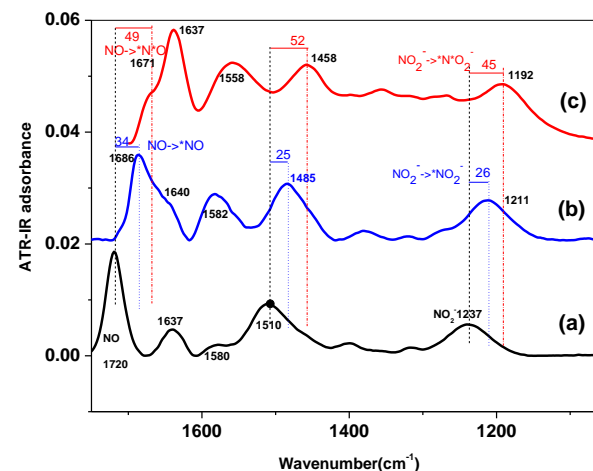


Fig1. ATR-IR spectra of nitrite adsorption over H-Pd/Al<sub>2</sub>O<sub>3</sub> (a) <sup>14</sup>N<sup>16</sup>O<sub>2</sub><sup>-</sup> (b) <sup>15</sup>N<sup>16</sup>O<sub>2</sub><sup>-</sup> (c) <sup>15</sup>N<sup>18</sup>O<sub>2</sub><sup>-</sup>

Further study of hydrogenation of nitrite adsorbed species by flowing H<sub>2</sub>/H<sub>2</sub>O shows a kinetic isotope effect, the rate of hydrogenation of various adsorbed species is influenced by the nitrite isotopes, hydrogenation of "NO(l)" species is follows the order <sup>15</sup>N<sup>18</sup>O<sub>2</sub><sup>-</sup> > <sup>15</sup>N<sup>16</sup>O<sub>2</sub><sup>-</sup> > <sup>14</sup>N<sup>16</sup>O<sub>2</sub><sup>-</sup>. In the presentation the new assignment of the IR peaks of adsorbed species as based on the isotopic shifts as well as the kinetics of hydrogenation of adsorbed species (not shown here) will be used to modify the hypothesis on the mechanism of nitrite hydrogenation reaction

## References

1. Noelia, Barrabes.; Jacinto, Sa. *Applied catalysis B; environmental*, 2011, 104, 1.
2. Burgi, Thoma.; Alfons, Baiker. *Advances in catalysis*, 2006, 50, 227.
3. Sune, D, Ebbsen.; Barbara, L., Mojet; Leon, Lefferts, *Journal of Catalysis*, 2008, 256,15.
4. T., E., Hoost.; K., Otto.; K, A, Laframboise.; *Journal of Catalysis*, 1995, 155, 303.
5. Konstantin I. Hadjiivanov.; *Catalysis Reviews: Science and Engineering*, 2000, 42, 71.