

Different surface species found by ATR-IR spectroscopy during nitrite reduction over Pt/Al₂O₃ and Pd/Al₂O₃

B.L. Mojet*, S.D. Ebbesen, L. Lefferts

Catalytic Processes and Materials, Faculty of Science and Technology, MESA+, University of Twente, P.O. box 217, 7500 AE, Enschede, The Netherlands,

*B.L.Mojet@utwente.nl

Introduction

Groundwater pollution by nitrite and nitrate is a widespread problem which has risen in the recent years throughout the world. Since high nitrite and nitrate concentrations in drinking water are dangerous to human health, technologies for their removal have to be developed and implemented. It is an important and developing area in environmental research. The most promising technique for nitrate and nitrite removal is the catalytic denitrification by noble metal catalysts [1]. Selectivity towards nitrogen is a key point in order to minimize the formation of ammonia, which is also toxic for humans, but deep insight in the mechanism is lacking.

Supported noble metal catalysts possess activity towards nitrite removal, where platinum and palladium were found to be the most active and selective towards nitrogen. It has been shown that the catalytic reduction of nitrate proceeds via nitrite as an intermediate. In addition, adsorbed NO was suggested to be the key intermediate on the noble metal surface [2], but so far no NOads was reported. As a first step in unraveling the nitrate hydrogenation mechanism, we investigated the hydrogenation of nitrite. In this work we show that Attenuated Total Reflection Infrared Spectroscopy (ATR-IR), is ideally suited for studying adsorbates on the catalyst surface running the reaction operando. ATR-IR results for nitrite reduction over Pt/Al₂O₃ and Pd/Al₂O₃ will be presented and discussed.

Materials and Methods

Thin catalyst layers of either Pt/Al₂O₃ or Pd/Al₂O₃ were immobilized on ZnSe Internal Reflection Elements (IRE). After calcination and reduction, the catalyst film was ready to be used. Catalyst details are given in Table 1. Attenuated Total Reflection Infrared (ATR-IR) spectra were recorded with a Tensor FTIR spectrometer (Bruker) at room temperature using a home built stainless steel flow through cell.

Table 1. Catalyst details

Catalyst	Metal content	Metal dispersion (%)	Layer thickness (μm)
Pd/Al ₂ O ₃	4.96 wt% Pd	0.45 ^a	5.0 ± 0.5
Pt/Al ₂ O ₃	5.0 wt% Pt	0.75 ^b	3.5 ± 0.25

^a Pd dispersion was determined by CO chemisorption assuming CO:Pt = 1.

^b Pt dispersion was determined by H₂ chemisorption assuming H:Pt = 1.

Results and Discussion

During flow of NO₂⁻(aq) over Pt/Al₂O₃, infrared bands evolved as shown in Figure 1. NO₂⁻(aq) was detected by a broad band at 1235 cm⁻¹, while NO₂(ads) on platinum was characterized by bands at 1304 cm⁻¹ and 1385 cm⁻¹. The latter two bands were stable during Ar/H₂O flow, while NO₂⁻(aq) was removed. Subsequent flow of H₂/H₂O reduces the adsorbed species, resulting in NO(ads), NH₄⁺ and N₂O.

Remarkably, similar experiments over Pd/Al₂O₃ showed that adsorption and reduction of nitrite results in different surface intermediates compared to Pt/Al₂O₃. Clearly on Pd/Al₂O₃, selectivity towards N₂ and NH₄⁺ is determined by two different intermediates: NO(ads) and NH₂(ads). For Pt/Al₂O₃ on the other hand, all products seem to originate from adsorbed NO(ads). Differences and similarities between adsorption and hydrogenation on both catalysts will be discussed.

Significance

ATR-IR is a valuable tool to study reaction mechanisms for heterogeneous catalyzed reactions in water. Despite many hypotheses published in literature, this study convincingly shows that nitrite reduction over Pt/Al₂O₃ and Pd/Al₂O₃ does not follow exactly the same mechanism. Moreover, it is the first time that surface species have been observed during in-situ nitrite hydrogenation, which opens a new world for studying heterogeneous catalyzed reactions in water.

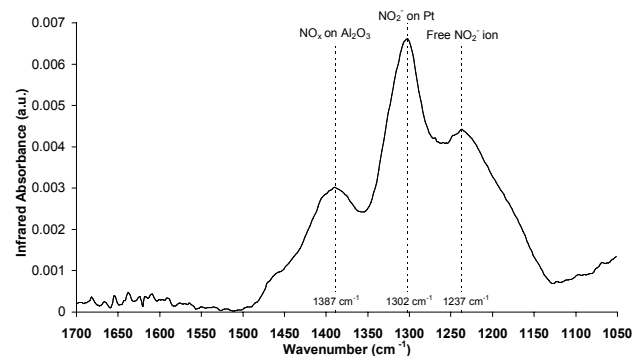


Figure 1. Water-corrected ATR-IR spectra showing adsorbed NO₂⁻ on Pt/Al₂O₃ while 200 ppm NO₂⁻ in water was flown.

References

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2. J. Wärnä, I. Turunen, T. Salmi, T. Maunula, *Chem. Eng. Sci.* 49, 5763 (1994).