DRIFTS-SSITKA and fast transient analysis of H_2-assisted NH3 SCR on Ag-alumina

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Introduction

Ag-alumina is a promising candidate for selective catalytic reduction (SCR) of NO_X for automotive applications. The co-feed of hydrogen together with the reducing agent makes the system active at low temperatures (200℃).

Objectives

This study aims at clarifying the reaction mechanism of H_2-assisted NH_3-SCR and the role of adsorbed NO_X as potential reaction intermediates. The objective is also to show the use of fast transients, Steady State Isotope Transient Kinetic Analysis (SSITKA) in combination with Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) and the subsequent spectral deconvolution using ALS in order to further improve the catalytic understanding.

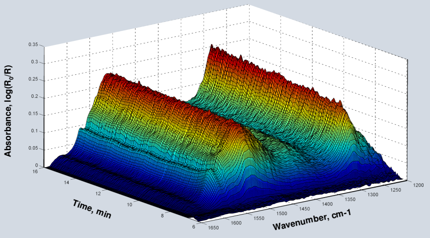

Figure 2a. Pulsing in ^{15}NO (5 pulses of 1 min starting from a pretreated catalyst) in a flow of 1000ppm NH_3, 1%H_2 and 5%O_2 (in Ar) at 180℃. The pulsing started as soon as peaks (from NH_3 feed) were observed. Surface plot of raw data from DRIFTS. The main spectral feature is NO_X that rapidly accumulates on the surface. Smaller changes with time can be seen, but are hard to further analyze using only raw data.

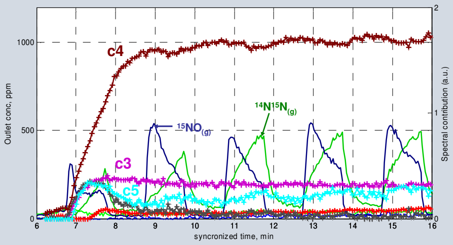

Figure 2b. Outlet gas phase concentrations together with ALS contributions corresponding to figure 2a. The formation of N_2 (as $^{14}N^{15}N$) is preceded by accumulation of component c3, c4, c5.

Alternating Least Squares (ALS)

By analysing DRIFTS data with ALS and plotting together with the gas phase concentrations it is possible to identify peaks that are potential SCR intermediates. The ALS procedure is a Latent Variable (LV) method: $\hat{\mathbf{X}} = \mathbf{C}\mathbf{R}'\mathbf{R}\mathbf{S}$ where

- **$\hat{\mathbf{X}}$ is the approximation of the spectra from PCA, using 5 components in this case,**
- **C are the contributions, corresponding to concentrations of adsorbed species,**
- **S is the matrix of pure spectra and**
- **R is a rotation matrix so that non-negativity constraints are obtained for both C and S.**

In order to improve the analysis, equality constraints on C and/or S can be imposed. By concatenating several experiments similarities between different experiments can be studied. For more about ALS c.f. [1].

In this study MATLAB 7 and PLS toolbox [2] was used.

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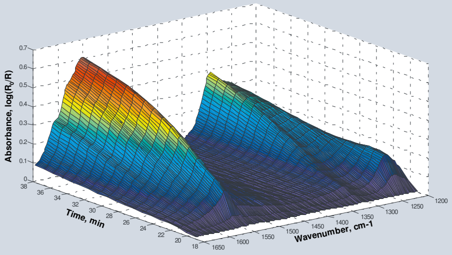

Figure 1a. NO-oxidation. 1000 ppm ^{14}NO in a flow of 5%O_2 (in Ar) at 250℃. Surface plot of raw data from DRIFTS. The main spectral feature is NO_X accumulation.

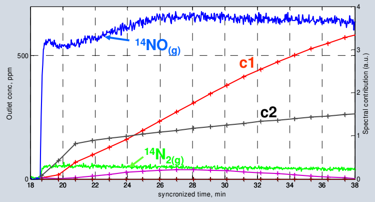

Figure 1b. Outlet gas phase concentrations together with ALS contributions corresponding to figure 1a. The step in NO feed (as ^{14}NO) is followed by accumulation of component c1 and c2. The corresponding pure spectra is displayed in figure 3.

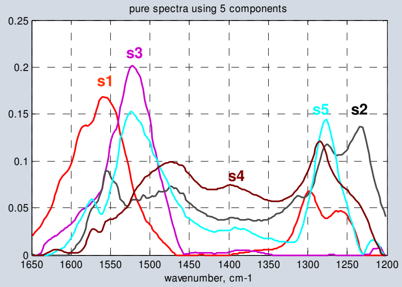

Figure 3. Pure spectra (S) from the ALS using 5 components. All 4 experiments (fig. 1, 2, 4, 5) were used simultaneously in the analysis. The different pure spectra may be interpreted as: species associated with ^{14}NO (s1-red, s2-black) and species associated with ^{15}NO (s3-purple @400℃, s4-brown @180℃ and s5-turquoise @245℃)

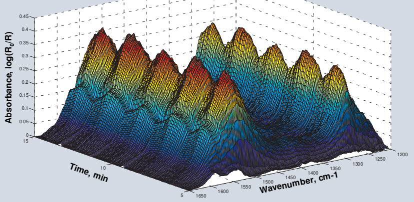

Figure 5a. Pulsing in $^{15}NO+^{14}NH_3$ (5 pulses of 1 min starting from a pretreated catalyst) in a flow of 1%H_2 and 5%O_2 (in Ar) at 245℃. Surface plot of raw data from DRIFTS. The main spectral feature is NO_X that rapidly accumulates on the surface, but varies with the pulsing.

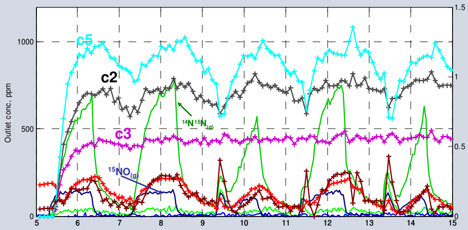

Figure 5b. Outlet gas phase concentrations together with ALS contributions corresponding to figure 5a. The formation of N_2 (as $^{14}N^{15}N$) is accompanied by all 5 components at different amplitudes, also those corresponding to $^{14}NO_X$.

References

[1] Tauler, R. (1995). Chemometrics and Intelligent Laboratory Systems 30(1), 133.

[2] http://www.eigenvector.com/

[3] He, H. (2008). Catalysis Surveys from Asia 12(1): 38-55.

[4] Breen, J. P. (2006). Topics in Catalysis V39(1): 53-58.

Acknowledgements

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Results

- **Using ^{15}NO and $^{14}NH_3$ as reactants, mixed nitrogen ($^{14}N^{15}N$) is the dominating gas phase product.**
- **The pure components spectra (fig 3) show features associated with nitrates/nitrites, e.g. [3]**
- **The contributions at 245℃ (fig 5) shows spectral features that increase at the same rate as N_2 production. At 400℃ (fig 4) as well as for 180℃ (fig2) the spectra is almost as fast as the N_2 production.**
- **Spectral feature associated with $^{14}NO_X$ is visible at 245℃ (red contribution, fig 5) indicating oxidation of ammonia.**

Discussion

- **Highly overlapping peaks due to complex system with small Ag clusters as well as "active" support (γ-alumina) makes spectral deconvolution challenging. Peak assignment would not be clear from this data set.**
- **The spectral features corresponding to candidate SCR intermediates are different for different temperatures, indicating the possibility for different sites for adsorbed NO_X, e.g. on metallic silver, on small silver clusters, on "active" alumina or on "storage-alumina" [3,4].**

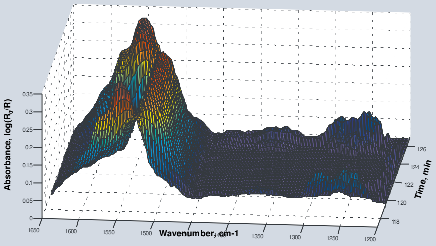

Figure 4b. SSITKA experiment switching between $^{14}NO/^{15}NO$ in a flow of 1000ppm NH_3, 1%H_2 and 5%O_2 (in Ar) at 400℃. Surface plot of raw data from DRIFTS. The main spectral feature is the isotope shift.

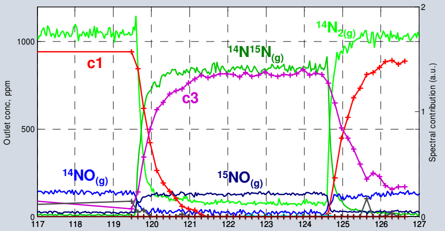

Figure 4b. Gas phase concentrations together with contributions from ALS corresponding to figure 4a. The production of N2 is rapidly followed by component c1 and c3.

Conclusions

- **The use of isotopes contributes to mechanistic understanding, e.g. $^{14}N^{15}N$ from ^{15}NO + $^{14}NH_3$.**
- **Nitrite/Nitrate is a probable reaction intermediate (or at least in fast equilibrium with intermediate)**
- **Spectral deconvolution using ALS improves the interpretation of DRIFTS data.**

Future work

- **Experimental design in order to better deconvolute spectral features**
- **Improved background treatments for temperature ramping experiments**
- **Inclusion of contribution into the fitting of kinetic models.**

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