In situ infrared study of NO_x reduction by NH_3

Responsible for the course: Oliver Kröcher (oliver.kroecher@psi.ch), phone: 056 310 20 66
Responsible of the TP: Marie-Gabrielle Ameres (marie-gabrielle.ameres@psi.ch), phone: 056 310 49 84

1. Objectives

- To familiarize with a setup for in situ spectroscopy (DRIFTS)
- To be able to summarize and analyze spectroscopy data in the form of tables and graphs
- To study the adsorption modes of ammonia on a V_2O_5/TiO_2 catalyst
- To compare the kinetics of consumption of adsorbed ammonia species with NO

2. Background

Selective catalytic reduction (SCR) is used to control NO_x emissions from diesel-powered vehicles and power plants. In this process, harmful NO_x is transformed into benign N_2 in the presence of a selective reductant such as ammonia (NH_3). The main reaction involved is termed "standard SCR" and proceeds according to Eq. 1.

$$4NO + 4NH_3 + O_2 \longrightarrow 4N_2 + 6H_2O \qquad \text{(Eq.1)}$$

Since they were introduced in the 1950s, V_2O_5/TiO_2-based materials have remained to be the most widely used SCR catalysts. Their commercial success stems from their high activity, good resistance to SO_2 poisoning, and moderate cost. In practice, WO_3 is added as a promoter to improve the activity and stability of the catalysts.

Infrared (IR) spectroscopy, especially if performed in *operando* and *in-situ* conditions, is a powerful technique to get insights into the reaction mechanism as it provides the possibility to monitor the catalyst surface (in terms of adsorbed molecule behavior) under reaction conditions. Information concerning adsorption sites, relative strength, stability, and geometrical arrangement, as well as the reactivity of adsorbed species involved in the reaction, can be obtained. Since the reaction implies a gas-solid interphase (gas-phase reactants and the solid catalyst surface), you are going to use Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS).

In this experiment, you will measure the spectrum of adsorbed ammonia on a V_2O_5/TiO_2 sample. You will have to identify the vibrational bands corresponding to ammonia bound to Lewis and Brønsted sites. After desorption of the excess of physisorbed and adsorbed ammonia, you will let the remaining ammonia react with NO to follow the reactivity of the adsorbed ammonia species and compare the kinetics of their consumption as a function of time.

3. Methods and materials

The experimental setup consists of a V_2O_5-WO_3/TiO_2 catalyst bed loaded into the sample holder of the DRIFT spectroscopic cell. The cell is attached inside the Praying Mantis (Harrick) accessory, which is then placed within the sample compartment of the IR spectrometer. The commercial Praying Mantis accessory consists of a set of mirrors of appropriate shapes and orientations to both direct the IR radiation from the source towards the catalyst surface, and to collect the diffuse radiation and direct it towards the detector. Since the detector is composed of Mercury Cadmium Telluride (MCT) it has to be cooled with liquid nitrogen. CAUTION: Wear a laboratory coat, goggles, and the special gloves for liquefied gases when handling liquid nitrogen. The spectroscopic cell possesses both inlet and outlet gas tubes. The former is connected to a system of multiple mass flow controllers and switching valves (to choose the inlet gas mixture and flow rate), while the latter to the exhaust. A schematic representation of the setup is shown in Figure 1. Figure 2, Figure 3 and Figure 4 display the laboratory setup, the DRIFT cell, and the Praying Mantis unit, respectively.

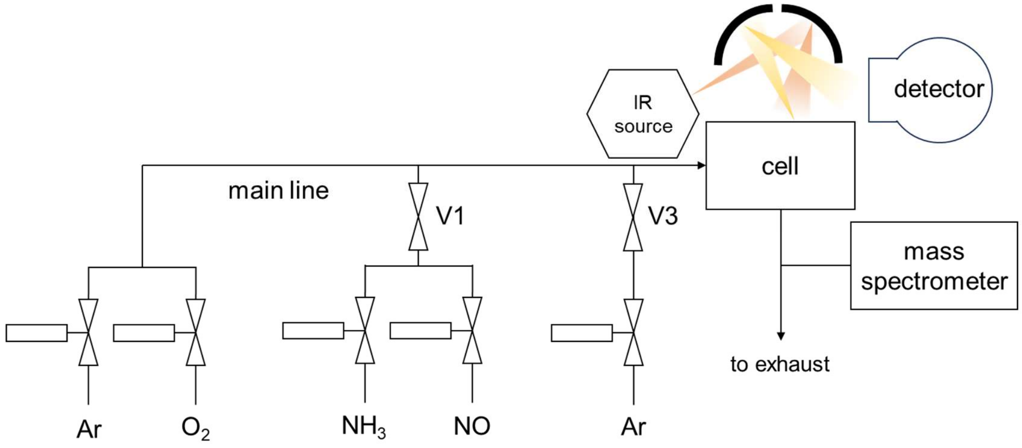

Figure 1: Schematic description of the employed experimental set-up

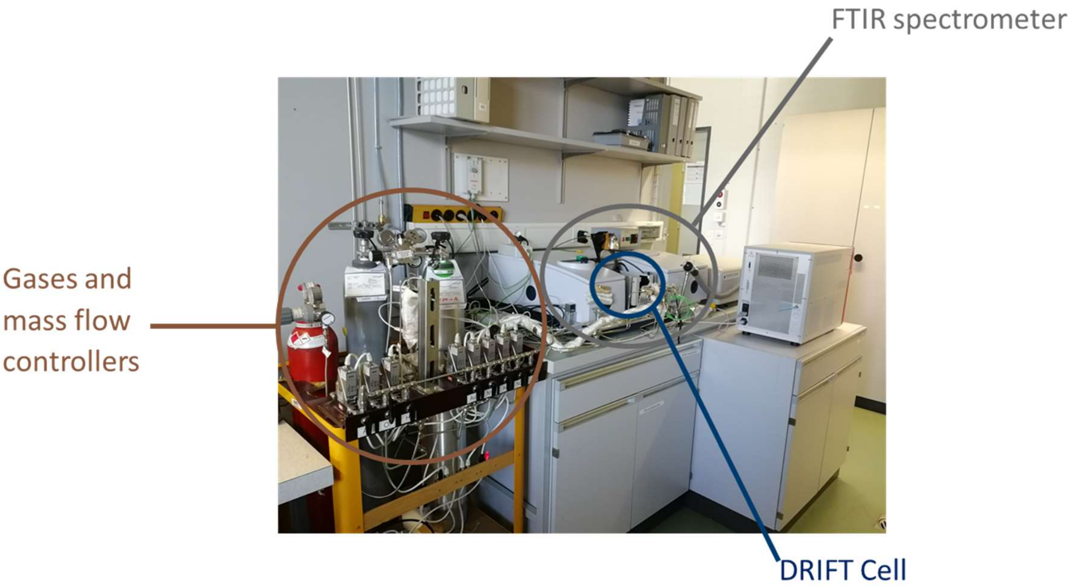

Figure 2: Experimental set-up

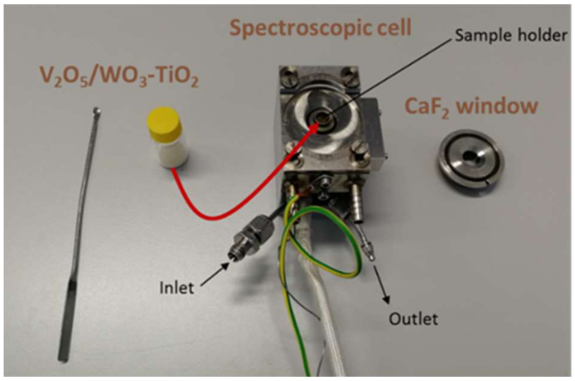

Figure 3: DRIFTS cell

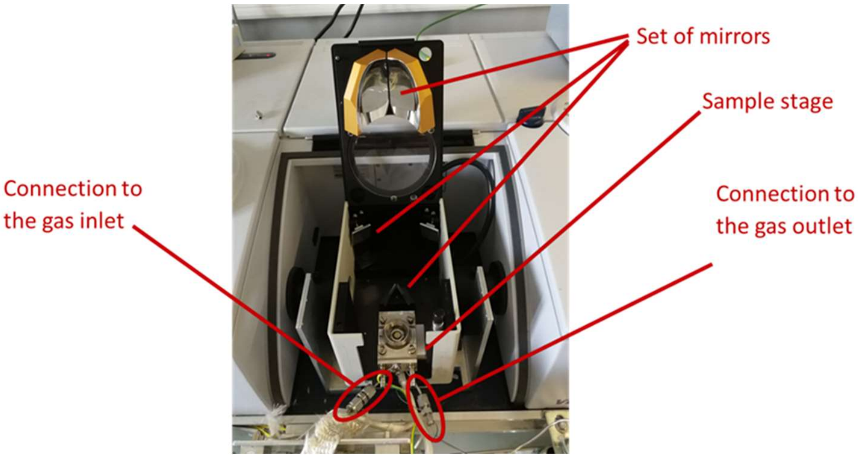

Figure 4: Praying Mantis accessory

4. Experimental procedure

The sample holder of the spectroscopic cell has to be properly loaded with the appropriate mass of V_2O_5-WO_3/TiO_2 catalyst powder, covered, secured within the sample stage of the FTIR spectrometer, and connected to the gas inflow and outflow tubing. Furthermore, the gas flow is set to 100 mL min^{-1} with a composition of 5 vol% O_2 in Ar. The cell is heated to 350 °C at a rate of 20 °C min^{-1} and maintained at that temperature for 30 min. This is needed both to activate the catalyst (V^{4+} to V^{5+}, catalyst active in the oxidized state) and to clean the catalyst surface for background measurement and successive adsorption experiments. Finally, the catalyst bed is cooled down to 250 °C.

After filling the detector with liquid nitrogen, a background spectrum (i.e. the clean catalyst surface containing hydroxyl and vanadyl groups) is recorded (20 scans, 80 kHz) to be subtracted from future spectra. During the analysis, the final IR spectra will be returned by the software upon subtraction from the spectrum of interest (i.e. catalyst surface and adsorbed species) the background spectrum (i.e. catalyst surface). Thus, if, during the analysis, gas species adsorb on the catalyst surface, these will be observed as positive absorbance signals, since they were not present on the clean catalyst surface (i.e. background). If, however, during the experiment, some features of the catalyst are consumed, negative peaks will appear in the IR spectrum.

The **ammonia adsorption** experiment is performed by collecting IR spectra every 5 s for 30 min, and by changing the gas composition to 1000 ppm NH_3/5 vol% O_2 in Ar after measuring the first three spectra. In this way, NH_3 will start adsorbing on Lewis and Brønsted acid sites present on the catalyst surface and different signals will appear in the spectrum. In both cases, stretching and bending vibrational modes will develop at high and low wavenumber values, respectively. Note that the signal of atmospheric $CO_{2,(g)}$ can also appear since the Praying Mantis apparatus is not sealed/under vacuum. (Data set name: IR-NH3-ads-O2-Ar-250C)

To observe **ammonia desorption**, IR spectra were again recorded every 5 s for 30 min, stopping the NH_3 flow by changing the gas composition to 5 vol% O_2 in Ar, after measuring the first three spectra. It is important to always maintain a steady-state value of the total flow rate inside the cell to avoid undesired effects on the recorded spectra. This experiment aims at understanding the relative stability of NH_3 adsorbed species on Lewis and Brønsted acid sites.

The weaker the interaction of a peculiar site with NH_3, the steeper will be the decrease of that signal over time. (Data set name: IR-NH3-des-O2-Ar-250C)

Reaction with NO is investigated next. The spectra are recorded every 5 s for 30 min. NO is flowed in after measuring the first three spectra by setting the gas composition to 1000 ppm NO/5 vol% O_2 in Ar. As in the previous experiment, the more reactive the NH_3 adsorbed on a specific site, the steeper will be the decreasing of that signal over time upon NO introduction. (Data set name: IR-NO-rxn-O2-Ar-250C)

More spectra are recorded to observe **NO desorption**, once again, every 5 s for 30 min, while terminating NO flow by setting the flow gas-phase composition back to 5 vol% O_2 in Ar. As it has been done in the NH_3 desorption experiment, here the aim is to understand the strength of interaction of NO with the catalyst surface. The weaker it is, the faster the intensity of the IR peak associated with the adsorbed species will decrease over time. (Data sets name: IR-NO-des-O2-Ar-250C)

5. Report

5.1. Plot the last spectrum collected in the IR-NH_3-ads-O_2-Ar-250°C dataset. Based on the existing information available in the scientific literature, assign the peaks associated with the adsorbed species. Which adsorbed species can you detect and on which adsorption site? Which of these adsorption sites are associated with V, W, and Ti?

5.2. Based on the previous plot, why are some IR peaks positive and some negative?

5.3. Plot the temporal evolution of the signals (normalized absolute area) associated with the adsorption sites for NH_3 in the IR-NH_3-des-O_2-Ar-250°C dataset. Comment on the relative stability of the NH_3 adsorption sites.

5.4. Plot the temporal evolution of the NH_3 adsorption sites (normalized absolute area) in the IR-NO-rxn-O_2-Ar-250°C dataset. Is there a difference in NH_3 consumption in the different adsorption sites?

5.5. Compare the first and the last spectra in the IR-NO-des-O_2-Ar-250°C dataset. What can you say about NO adsorption on the catalyst?

5.6. How can you use the information you obtained from IR spectroscopy to develop a more active SCR catalyst?

6. References

A. Marberger, D. Ferri, M. Elsener, O. Kröcher, *The significance of Lewis acid sites for the selective catalytic reduction of nitric oxide on vanadium-based catalysts*, Angew. Chem. Int. Ed. 55 (2016) 11989.

7. Notes

The data sets you will have to analyze present a .dpt extension. They contain a series of data columns. The first one represents the wavenumber range in which the IR spectrum has been collected. From the second to the last column the absorbance of the IR signal at that precise wavenumber value is reported during time (already background substracted). Each of these columns, thus, represents the IR spectrum at a different time. The most straightforward way to plot and analyze these data is by using Origin as software. Just drag and drop the .dpt file of interest in the origin window and a book of data will be created. Spectra have to be reported as absorbance vs wavenumber as displayed in the examples below.

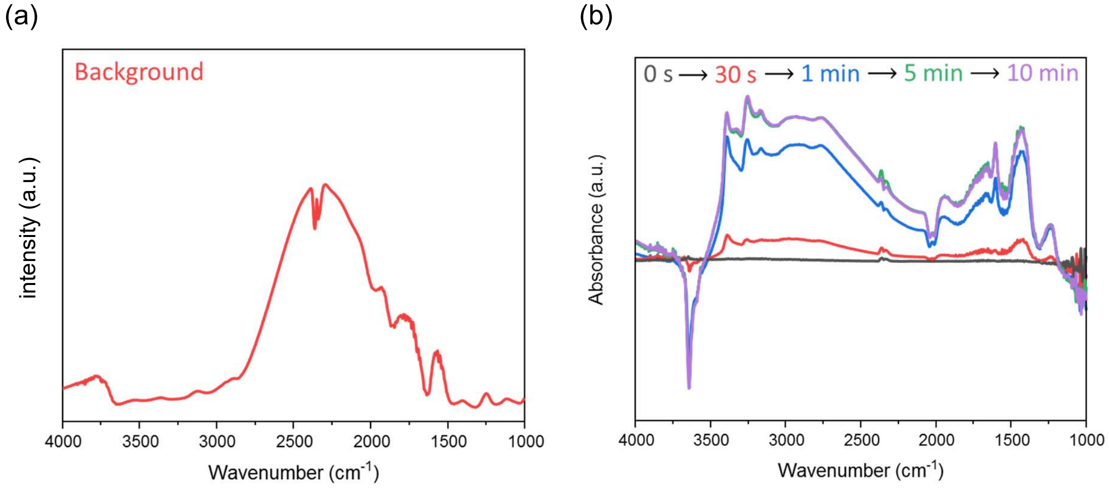

Figure 5: a) Background IR spectrum of the V_2O_5-WO_3/TiO_2 catalyst b) IR spectra recorded during the NH_3 adsorption experiment