

## In Situ Characterisation of Heterogeneous Catalytic Reactions by Raman and IR Vibrational Spectroscopies on a single Instrument

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### Complementary IR and Raman spectroscopies for the study of catalytic reactions

A catalyst is a chemical species able to increase the speed of a thermodynamically allowed reaction. If many reactions are likely to occur, a well selected catalyst may selectively increase the speed of a given reaction at the expense of the other reactions. Catalysts are therefore of great interest to the industry as they allow to improve yields and to better tune the properties of the final product.

Vibrational spectroscopic characterisation can take place all along the catalyst life from the control of the synthesis of the precursor to the control of the catalyst regeneration via the analysis of the surface reaction mechanism. To study catalytic reactivity, the strengths of Raman include the higher spatial resolution and the ability to probe the low wavenumber spectral range where most of the active phases (metal oxides or sulfides) have their characteristic lines. Thus Raman spectroscopy has been applied in heterogeneous catalysis for the characterization of bulk and supported oxides. As a complementary technique, FTIR has been more widely used for the characterisation of the surface acidity of the catalysts through the adsorption of probe molecules (1).

The FTIR/Raman combination microprobe system, using SameSpot™ technology enables simultaneous examination of one sample area by both techniques. A single microscope is simultaneously coupled to a Raman spectrograph and an infrared interferometer. While the spatial resolution is quite different because of the diffraction limit imposed by the wavelength of the probing radiation, the laser and IR beams coincide at the sample, thus providing information on essentially the same material area.

Taking advantage of the different information available from the two techniques, this new technology enables the characterisation of on-going heterogeneous catalytic processes by using a dedicated cell directly fitted to the microscope stage. The ability to monitor the very same reaction via both techniques in a quasi-simultaneous approach provides full and complementary vibrational information about the mechanisms involved at the surface of the catalyst during a catalytic reaction.

This new technological improvement enables us, as an example of application, to follow both the modification of the molecular structure of the active phase by Raman spectroscopy with a 633nm laser excitation line and the nature of the different surface adsorbed reaction intermediates by IR spectroscopy during the reaction of NO decomposition at 473 K on an alumina supported palladium.

### Simultaneous IR and Raman study of a catalytic reaction: Experimental

#### 1. In situ Raman and FTIR quasi-simultaneous spectroscopic measurements

Raman and FTIR spectroscopic measurements were performed on a **LabRAM IR** spectrometer. This instrument is a combined dispersive Raman and FT-IR microscope. An all-reflecting objective (Cassegrain/Schwarzschild type) as shown in Fig. 1 enables both Raman and FTIR spectra to be acquired. Indeed, this optical system has been specifically designed and optimised to provide an additional unique functionality to the LabRAM IR : the collection of Raman and IR spectra from the same spot without any need for switching objectives. This greatly facilitates the operation and handling of the samples.

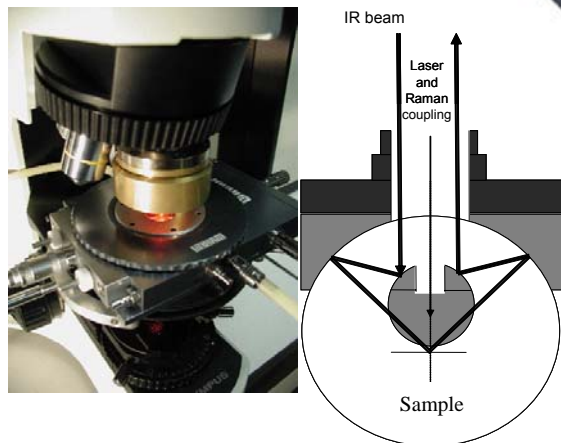


Figure 1. Picture of the in-situ device and schematic representation of the Cassegrain objective with both laser (He/Ne 633nm) and IR beams.

## 2. Description of the dedicated Cell

Powdered catalyst was placed in a Linkam stage directly adapted to the microscope of the instrument, which provides controlled atmosphere and temperature.

The window of the cell was made of ZnSe and was 1 mm thick. ZnSe was selected because of its high transmission in the infrared, and its total inertness under the working conditions. Although ZnSe exhibits a rather intense Raman spectrum below  $350\text{ cm}^{-1}$  (Figure 2A), possible interferences of these features with the signal of interest could be avoided by using the confocality of the microscope. Indeed, the confocal principle allows one to select a restricted collection volume by filtering out the signal coming from out-of-focus or adjacent regions. As shown in Figure 2B, the  $\text{MoO}_3$  spectrum is well resolved and no contribution of the ZnSe window is observed.

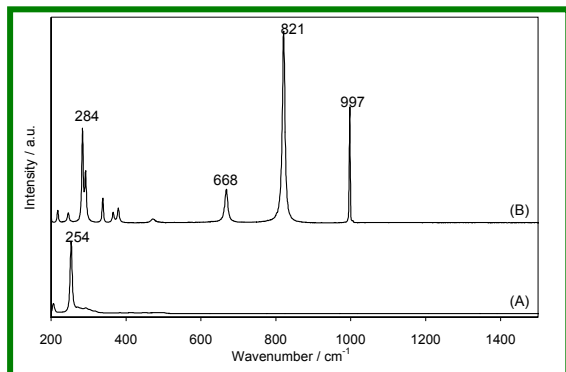


Figure 2. Raman spectra of (A) ZnSe window material and of (B) molybdenum oxide introduced in the cell.

## Study of the heterogeneous solid-gas DeNO<sub>x</sub> catalytic reaction

Thus the mechanism of the catalytic DeNO<sub>x</sub> reaction on supported metal particles can be studied. DeNO<sub>x</sub> reaction is an heterogeneous catalytic process aiming to eliminate nitrogen oxide gas by reduction on the surface of metal particles. The catalyst used was a commercial  $\gamma$ -alumina supported Pd/ $\text{Al}_2\text{O}_3$ . Complementary IR and Raman information on the catalytic system at steady state can be obtained quasi simultaneously on the LabRAM IR system.

This allowed us to identify the intermediate species and the poisoning ones in order to better understand gas- surface interactions and to optimize catalysts morphology and composition. Moreover, the evolution of the supported active phase during the reaction can be monitored by Raman spectroscopy (2) whereas, due to the strong absorption of the catalytic support, such information is not available from IR studies in the low wavenumber spectral range.

Both Raman and IR spectra were recorded *in situ* during the NO reduction. Assignments of the Raman and IR bands have been done respectively by reference to previous study (2) and to literature data (5-9). Raman and IR spectra are reported respectively in Figures 3 and 4. A very small contribution from the ZnSe material of the window appears in the low wavenumber part of the Raman spectrum but thanks to a decrease of the size of the confocal hole this line can be eliminated, which avoids any interferences with the Raman signal of interest.

### Before activation treatment

The **Raman spectrum** in Fig. 3A obtained on a sample directly introduced in the cell exhibited a major Raman line at  $639\text{ cm}^{-1}$ , assigned to palladium oxide (3), which underlines a **slight surface oxidation of Pd (PdO)** after contact with air at room temperature. In parallel, we observed in the **IR spectrum** (Fig. 4A) the presence of **adsorbed water** ( $1649\text{ cm}^{-1}$ ) and **carbonate species** ( $1509$  and  $1401\text{ cm}^{-1}$ ) **on alumina** (4).

After  $H_2$  reduction at 573 K for 2 hours

The infrared data (Fig. 4B) showed that formerly adsorbed water and carbonate

species were desorbed after the treatment while the Raman features of PdO are no longer observed (Fig. 3B). Such observations suggest the cleanness of the catalyst surface and the reduction into metallic Pd.

As soon as the catalyst has been exposed to NO at 473 K,

the infrared spectrum (Fig. 4C) exhibits bands at 1461 and 1561  $cm^{-1}$  assigned to chelating bidentate nitrito ( $-O_2N$ ) compounds (Fig. 5i).

Simultaneously, the Raman spectrum (Fig. 3C) exhibited a line at 1049  $cm^{-1}$  attributed to the presence of nitrate species (Fig. 5iv) adsorbed on alumina and two lines at 828 and 1308  $cm^{-1}$  assigned to nitro compounds (Fig. 5v).

After one hour exposure to NO,

the apparition of a new set of infrared bands at 1556  $cm^{-1}$ , 1614  $cm^{-1}$  and 1305  $cm^{-1}$  (Fig. 4D) characterizes the formation of nitrate species: bidentate nitrate ( $-O_2NO$ ) compounds (Fig. 5ii) and bridged nitrate compounds (Fig. 5iii).

After cooling under NO to 298 K,

We could clearly notice changes in the IR spectrum (Fig. 4E) that can be attributed to the formation of nitro compounds ( $-NO_2$ ) (Fig. 5v). In Raman spectroscopy, the lines previously assigned to nitro species were no longer observed in the spectrum (Fig. 3E) whereas new lines can be attributed to nitrate species.

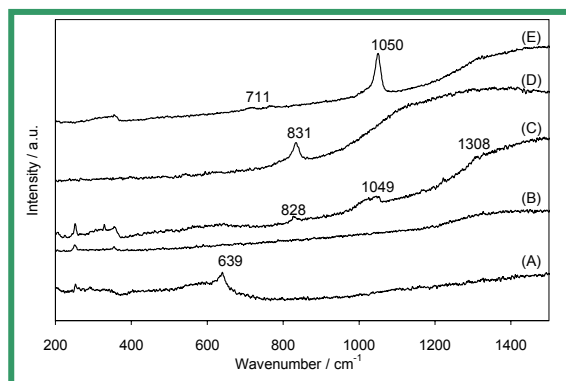


Figure 3. In situ Raman spectra (633nm excitation line) obtained on (A) a 1 wt. % Pd/ $\gamma$ - $Al_2O_3$  exposed to air at room temperature, (B) after reduction under  $H_2$  at 573 K for 2h and after  $5 \times 10^{-3}$  NO atm exposure at 473 K (C) for 30 mn, (D) for 1 hour, and (E) after cooling down to room temperature under NO flow.

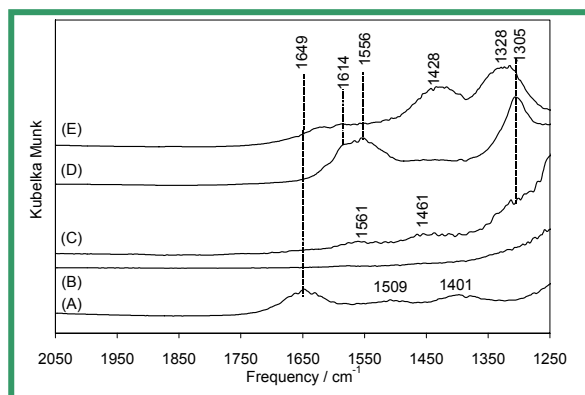


Figure 4. In situ IR spectra obtained on (A) a 1 wt. % Pd/ $\gamma$ - $Al_2O_3$  exposed to air at room temperature, (B) after reduction under  $H_2$  at 573 K for 2h and after  $5 \times 10^{-3}$  NO atm exposure at 473 K (C) for 10 mn, (D) for 1 hour, and (E) after cooling down to room temperature under NO flow.

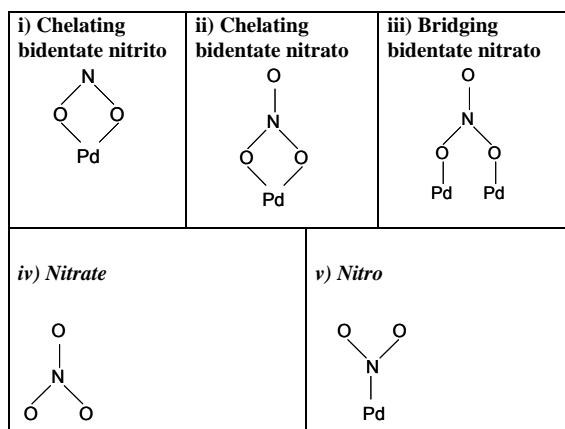


Figure 5. Structure of surface NO<sub>x</sub> species.

### Conclusion

Simultaneous *in situ* Raman and FTIR spectroscopic characterisations of catalytic systems under reaction conditions have been successfully performed with the LabRAM IR using a dedicated cell. Different adsorbed NO<sub>x</sub> species (nitrito, nitrate, nitro and nitrate compounds) on the surface of the alumina supported palladium during NO exposure at 473 K have been identified by these spectroscopic measurements.

These measurements highlight the complementarity of the two techniques for investigating catalytic reactions. Indeed, Raman spectroscopy gives access to information located at low wavenumbers, enabling the characterization of the active phase during the reaction, while the high sensitivity of IR spectroscopy allows probing adsorbed species at low concentration.

### References

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