Application note

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Analysing catalytic powders with the Virsa™ Raman analyser

Virsa Raman analyser

Renishaw's Virsa Raman analyser is a transportable fibre-coupled system that is well suited to identifying chemicals and determining the phase and crystal structure of materials.

Vanadium oxide

Vanadium oxide is a common catalytic powder used as an industrial catalyst in the production of sulphuric acid as well as other industrial chemicals. Vanadium oxide occurs in 52 stable and metastable phases. Of these V_2O_5 is most effective for the production of sulphuric acid. High purity cost effective synthesis routes of V_2O_5 are under investigation, but these often yield other phases. The presence of phase impurities is undesirable for sulphuric acid production but can be suitable for other catalytic reactions.

In this study we used the Virsa Raman analyser to identify the chemical phase of vanadium oxide to aid the screening and evaluation of different production methods.

Advantages of the Virsa analyser

The Virsa Raman analyser has many features that make it ideal for this type of analysis:

- Flexible fibre-based probes allow measurements to be conducted on large volumes of powder without the need for any preparation. This also enables *in situ* measurements of the powder during production and when used as a catalyst.
- The optional SB100 motorised three-axis stage and video unit enable you to precisely position the probe. This makes it easy to navigate your sample and focus on the area of interest.
- The SB100 stage enables Raman mapping, so you can study the heterogeneity of your samples.
- The Virsa analyser can measure low wavenumber bands (it has a 50 cm^{-1} filter edge as standard). It can detect the bands below 100 cm^{-1} from vanadium oxide, for example.
- It has better than 2.5 cm^{-1} spectral resolution, enabling it to accurately determine the shape and position of Raman bands. This is vital for distinguishing closely related chemicals.
- You can finely control laser power, in 0.1 mW increments. This is especially useful when analysing samples prone to laser induced changes, such as the oxides of vanadium.
- It has high sensitivity, even when used with low laser powers, so can successfully study thin films, weak scatterers, and samples prone to laser-induced changes. It can even measure the 4^{th} order silicon band, an exceptionally challenging test normally only achievable on laboratory microscope-based systems.

Raman analysis of bulk vanadium oxide powders

We examined two different vanadium oxide samples produced by a novel proprietary process. The aim was to determine whether the different processing conditions of the two samples produced different polymorphs (or polymorph mixtures). These powders were semi-crystalline and had broad bands and low Raman scattering intensities, making analysis more challenging. Identification was made using data available in the comprehensive work by Shvets, Petr, et al. “A review of Raman spectroscopy of vanadium oxides.” **Journal of Raman Spectroscopy** 50.8 (2019): 1226-1244. It should be noted that in all cases it seems unlikely that pure samples were produced and instead the dominant species in each spectrum is discussed.

One of the key challenges was the sensitivity of the samples to change brought about from high laser power densities. Excessive laser powers causes the vanadium oxide to melt, sinter, recrystallise and often change phase. An example of this is shown in Figure 2. Here it can be seen that by increasing the power on the sample from 1.1 mW to 1.8 mW the vanadium oxide bands sharpen as a result of temperature induced annealing and recrystallising. Increasing the power further to 2.3 mW results in a phase change from V_6O_{13} to a mixture of α- V_2O_5 and β-V_2O_5.

This highlights the need for precise laser power control on the sample; subsequent measurements were all conducted at 1.1 mW.

We Raman mapped each of the samples to determine which polymorphs were present and examine their uniformity. Figure 3 shows an optical image illustrating the typical sample surface along with measurement locations for Sample 1. The Raman spectra (Figure 4) showed that Sample 1 consists of a mixture of polymorphs (with differing orientations), with the analysis points exhibiting different spectra and therefore indicating the presence of different compositions. In contrast Sample 2 was more uniform and primarily consisted of V_6O_{13}. This difference in homogeneity is important as it has an impact on the catalyst’s efficacy. In Sample 2 the spectrum from one of the sampled positions has a broad band centred on 80 cm^{-1} which can only be seen because of the Virsa Raman analyser’s 50 cm^{-1} filter edge.

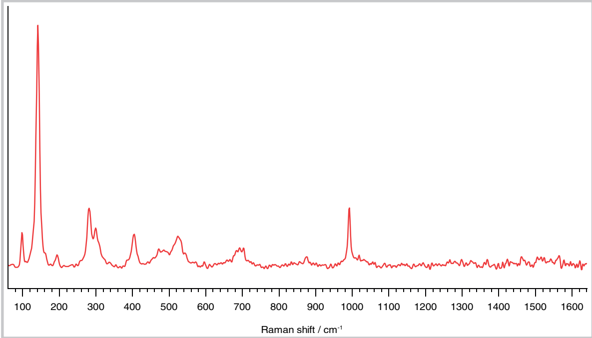

Figure 1 - Raman spectrum of highly crystalline α-V_2O_5. Data was collected using a 532 nm laser excitation source, with 2.3 mW laser power at sample and an acquisition time of 60 seconds.

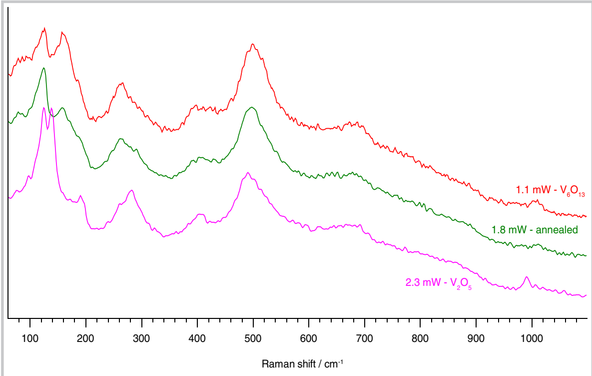

Figure 2 - Raman measurements of a vanadium oxide powder sample conducted with a 532 nm laser excitation source using three different laser powers. The spectra show that the material is transforming under higher laser powers.

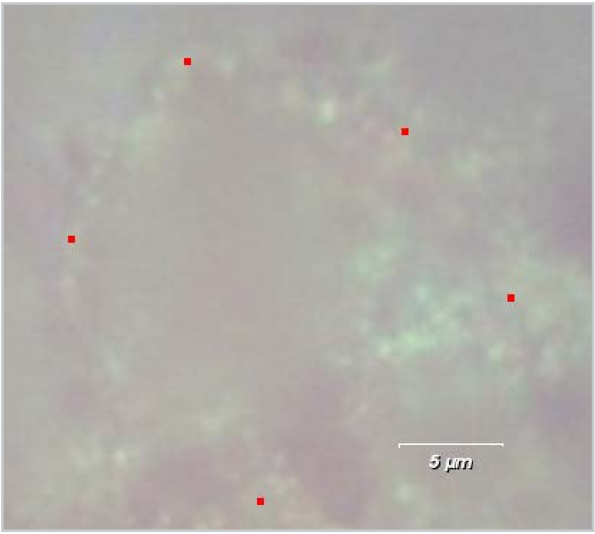

Figure 3 - An optical image of Sample 1 illustrating the measurement locations.

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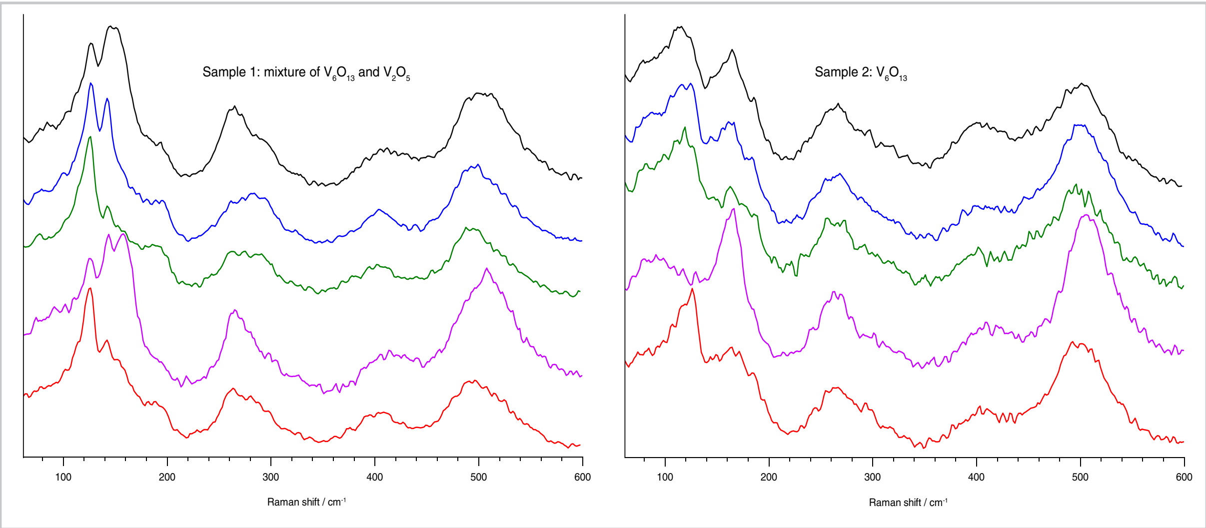

Figure 4 - Raman spectra collected from 2 samples of Vanadium oxide powder prepared using different methods. Measurements were conducted using a 532 nm laser source with 1.1 mW of power at the sample and 60 second measurement times.

Summary

- The Virsa Raman analyser is a powerful tool for the chemical analysis of powders because of its high sensitivity and flexible sample handling capabilities.
- It can be used to differentiate between different polymorphs and phases of materials.
- You can obtain high quality spectra from challenging samples quickly and with low laser powers.
- The Virsa Raman analyser is compact and transportable so measurements are no longer restricted to the laboratory but can be collected *in situ* at the process line.

A range of related Renishaw literature is available. Please ask your local Renishaw representative for more information.

Renishaw. The Raman innovators

Renishaw manufactures a wide range of high performance optical spectroscopy products, including confocal Raman microscopes with high speed chemical imaging technology, dedicated Raman analysers, interfaces for scanning electron and atomic force microscopes, solid state lasers for spectroscopy and state-of-the-art cooled CCD detectors.

Offering the highest levels of performance, sensitivity and reliability across a diverse range of fields and applications, the instruments are designed to meet your needs, so you can tackle even the most challenging analytical problems with confidence.

A worldwide network of subsidiary companies and distributors provides exceptional service and support for its customers.

Please visit www.renishaw.com/virsa for more information.