

Looking Inside Catalyst Extrudates with Time-Resolved Surface-Enhanced Raman Spectroscopy (TR-SERS)

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Raman spectroscopy is one of the major characterization methods employed over the last few decades as a nondestructive technique for the study of heterogeneous catalysts and related catalytic reactions. However, the promise of practical applicability on millimeter-sized catalyst bodies, such as extrudates, has not been fulfilled completely. Large fluorescence signals and the highly scattering nature of the extrudates often hamper its practical usage. Different approaches to overcome this problem were examined, including the use of time-resolved Raman spectroscopy (TRRS), spatially offset Raman spectroscopy (SORS), surface-enhanced Raman spectroscopy (SERS), and combinations of these techniques. This paper demonstrates that especially TRRS can provide chemical information at depth within catalyst bodies, overcoming fluorescence background signals and allowing for visualization of analytes at different depths. It also examines the application of time-resolved SERS within catalyst bodies to gain insight into localized activity. With these options a wider applicability of Raman spectroscopy for industrial catalysis research becomes within reach.

Index Headings: Heterogeneous catalysis; Depth profiling; Time-resolved Raman spectroscopy; TRRS; Spatially offset Raman spectroscopy; SORS; Surface-enhanced Raman spectroscopy; SERS.

INTRODUCTION

Heterogeneous catalysis is a vital field of research for many industries; it has been estimated that 90% of all chemical processes use heterogeneous catalysis, encompassing important industrial reactions from oil cracking and synthesis of transportation fuels to the production of plastics.¹ Catalytic solids in industrial reactors are often used under high pressure, where if the catalyst does not have a high mechanical stability it can compact and lead to blockages in the system. For this reason, porous catalyst support materials, such as Al₂O₃, TiO₂, and SiO₂, are often shaped into extrudates, which present a high surface area for catalytic reactivity, while retaining high mechanical stability under pressure.^{2–4} It is of particular interest in catalysis to determine whether reactants and products, as well as the catalytic activity and selectivity, are evenly distributed within catalyst bodies. Equally important is the extent to which the activity of the catalyst bodies is hindered by the deposition of byproducts within the extrudates.^{5,6}

A range of invasive and noninvasive techniques, encompassing ultraviolet-visible-near-infrared (UV-Vis-NIR), infrared (IR) spectroscopy, Raman spectroscopy (RS), magnetic

resonance imaging (MRI), and others, has been utilized in the past to visualize catalyst preparation methods. At the same time, RS, MRI, and X-ray techniques have been used to gain insight into in situ processes in extrudates.^{7–9} These techniques have revealed important information about the dispersion of the active sites within an extrudate, enabling studies of catalytic reactions on extrudates. However, noninvasive in situ measurements for single catalyst extrudates, allowing the monitoring of a reaction below the surface, have thus far only been done by MRI and diagonal offset Raman spectroscopy (DORS), the latter e.g., to study the preparation of Mo/Al₂O₃ catalyst bodies.^{9,10}

Raman spectroscopy is especially attractive as it provides valuable structural information, while the technique is nondestructive and does not require invasive sampling. It has been used to study chemical reactions on the surface of catalyst bodies,^{11–13} but a major problem in characterizing real extrudates is the large fluorescence background often encountered in catalytic solids. This makes analysis inside extrudates extremely challenging, especially since the pellet material is normally highly scattering. Surface-enhanced Raman spectroscopy (SERS), spatially offset Raman spectroscopy (SORS), and time-resolved Raman spectroscopy (TRRS) are all advanced Raman techniques that have been introduced, in part, to overcome the problem of fluorescence interference in a variety of applications.^{14–20} Through signal enhancement and selectivity for material in the bulk versus the surface, these methods could also help in studying the inside of catalyst extrudates in more detail.

The SERS effect is related to contact of the analyte with roughened metal surfaces or metal nanoparticles that enhances the signal by a factor of 10⁶ or more. The enhancement is based on both physical and chemical phenomena.^{14,15,21} SERS also effectively quenches the fluorescence of the adsorbed material by an increase in non-radiative decay when the molecule is in direct contact with the metal, which process is in competition with the radiative decay that gives fluorescence.²² For in situ measurements, selection of either Au or Ag SERS particles and selection of the appropriate excitation wavelength can be applied to avoid interference with the catalytic process. It will also be possible in future studies to utilize shell-isolated nanoparticles (SHINs) as chemically inert SERS probes.²³

The SORS technique allows depth measurements by applying a spatial offset between the excitation point and the Raman collection point.¹⁸ Scattering by opaque material causes a diffuse distribution of photons at depth, so a detector positioned at a location offset from the excitation point receives a relatively greater proportion of photons from deeper within the sample. Applying a spatial offset means that less signal is

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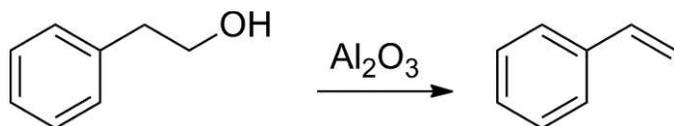


FIG. 1. Schematic showing the structures of reactant and product; 1-phenylethanol is dehydrated to styrene, using γ - Al_2O_3 as the active catalyst material.

collected from the location at which the beam enters the sample, thereby reducing the interference from fluorescence produced at the surface of the sample. Recently it has been shown that SERS used in combination with SORS can provide selectively enhanced depth measurements through diffusive surface layers for biomedical applications.^{24–26}

Time-resolved Raman spectroscopy by means of a Kerr gate¹⁶ or an intensified charge-coupled device (CCD) camera^{20,27–29} offers an alternative for sub-surface analysis inside a strongly scattering sample. With this approach the distinction between Raman photons emanating from the surface versus those generated inside the sample is made on the basis of their distribution in time. A picosecond (ps) laser pulse is used to excite the sample in backscattering geometry. Due to the random walk of photons in a dispersive medium, photons from inside the material will take longer to arrive at the detector. The use of a short detector gate allows selective collection of Raman photons from a certain depth within the sample and eliminates a considerable amount of fluorescent background from the surface as well as from the bulk.^{17,19,20}

Combinations of SERS, SORS, and TRRS are also possible. Previous work has shown that a slight improvement of the selectivity for photons from the bulk versus the surface can be achieved by combining TR detection with a SORS excitation geometry.^{27,29} However, the majority of fluorescence background reduction in TR-SORS is provided by the time gating rather than the spatial offset.^{27,29} Adding TR detection to SERS has the potential to be the basis of a selective, sensitive, and versatile tool for the study of chemical reactions in numerous applications as well. In this work, it is examined whether any of the above options can visualize the content in the core of an intact extrudate.

A model system is used that is representative of a catalytic system: styrene synthesis with γ - Al_2O_3 as the catalyst.^{30,31} The different components of this relevant reaction (Fig. 1) are added to γ - Al_2O_3 catalyst bodies as they are used in production. The spatial distribution of the starting compound (i.e., 1-phenylethanol) and product (i.e., styrene) is not known under normal catalytic conditions, but it is likely to be highly overlapping. To test the strengths of the various advanced Raman approaches, we chose to distribute these compounds unevenly within the catalyst body in a core-shell distribution model. Such systems are realistic in catalytic applications,⁵ and in doing so it is possible to determine not only the fluorescence suppression efficiency, but also the spatial selectivity of the different Raman approaches.

The spectral interference in this reaction normally comes from the formation of highly fluorescent polycyclic aromatic hydrocarbons, which are typical reaction by-products. Here, benzo[*a*]pyrene (BaP) is chosen as a typical example. The fluorescent lifetimes of these byproducts are generally such that TRRS can significantly reduce their contribution in the Raman spectra, regardless of their distribution within the sample. It

should be noted that when fluorescent byproducts are distributed throughout the bulk, SORS will not be as suitable, as the weak Raman signal will still be overwhelmed by fluorescence, irrespective of the spatial offset. Although in this study fluorescent interference from BaP only originates from the outer shell of the sample, the extrudate gives a significant luminescent background by itself. This creates a realistic situation in which multiple sources of fluorescence interference are present.

To study the contribution of SERS enhancement, a second model system was used. Again an uneven core versus shell analyte distribution was used, in which the core of the γ - Al_2O_3 extrudate was impregnated with rhodamine 6G (Rh6G), the golden standard for SERS enhancement.³² It should be noted that for many other compounds, including 1-phenylethanol and styrene, the enhancement factors with Ag nanoparticles are often much lower or more challenging to obtain.^{33–35}

EXPERIMENTAL

Instrumentation. The TRRS experiments were carried out with a system similar to the setup described in prior publications,²⁷ and it is schematically shown in Fig. 2. A tuneable Ti:sapphire laser (Coherent Mira 900P) was tuned to 920 nm and used in combination with a frequency doubler/tripler (TP-2000B, u-Oplaz) in second-harmonic generation (SHG) mode to reach nonresonant excitation at 460 nm. The pulse width was 3 ps and the system was operated at a 76 MHz repetition rate, with power at the sample of ~ 40 mW, or an approximate pulse energy of 0.5 nJ. The excitation beam is directed onto the sample with an approximate diameter of 120 μm . This is done at a 90 degree angle via a small prism (5 mm diameter) that can be displaced parallel to the sample surface to create a spatial offset relative to the static collection optics. Raman signal is collected in backscatter mode via Lens 3 (38 mm diameter, *f*/5). The Raman collection spot size is of the order of 0.5 mm.

For TRRS, an intensified CCD camera (La Vision Picostar) with a measurement gate width of approximately 250 ps is used.¹⁹ Initial gate opening is set to overlap with the laser pulse (t_0), and for subsurface measurements, the 250 ps gate is shifted in time after the laser pulse by increasing the gate delay. In this study, 25–50 ps steps were taken to obtain depth profiles. A conventional CCD camera (DV420-OE, Andor) is mounted to the same spectrograph for continuous wave (CW) RS and SORS experiments.

Materials. Chemicals used included styrene (Acros, 99%); 1-phenylethanol (1-P) (Aldrich, 97%); benzo[*a*]pyrene (BaP) (Acros, 98%); ethanol (Interchem, 100%); rhodamine 6G (Sigma, 95%); MilliQ ultrapure water (18.2 M Ω ·cm); silver nitrate (Sial, 99+%); and trisodium citrate dihydrate (Acros, 99%).

Silver (Ag) nanoparticles were synthesized using method *c* of Lee and Meisel, 1982.³⁶ The nanoparticles were centrifuged at 3300 RCF for 30 min, after which the supernatant was discarded and the particles were re-dispersed to 10 \times the initial concentration in demi-water.

The γ - Al_2O_3 extrudate pellets are “Al 3996 R” from Harshaw (bulk density 0.5–0.75 g/cm³, specific surface 200 m²/g, total pore volume approximately 0.69 cm³/g); the cylindrical hollow extrudate pellet is 3 mm in diameter, with a cavity of 1 mm diameter in the center. This cavity is filled with γ - Al_2O_3 extrudate spheres of Engelhard; the diameter of

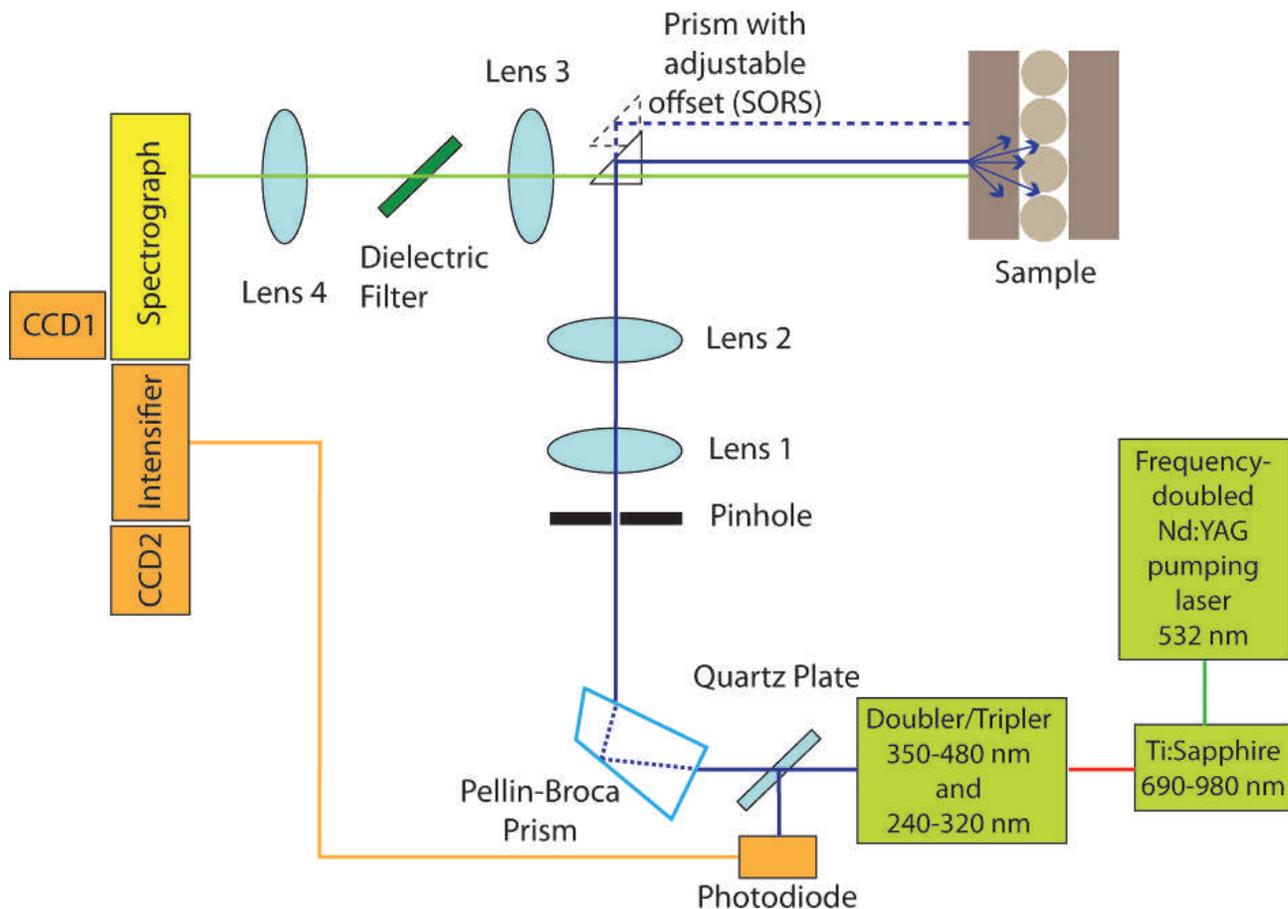


FIG. 2. Schematic showing the optical instrument capable of performing continuous wave (CW) RS and SORS (CCD1), as well as TRRS and TR-SORS (intensifier + CCD2). Excitation wavelength applied in this work was 460 nm.

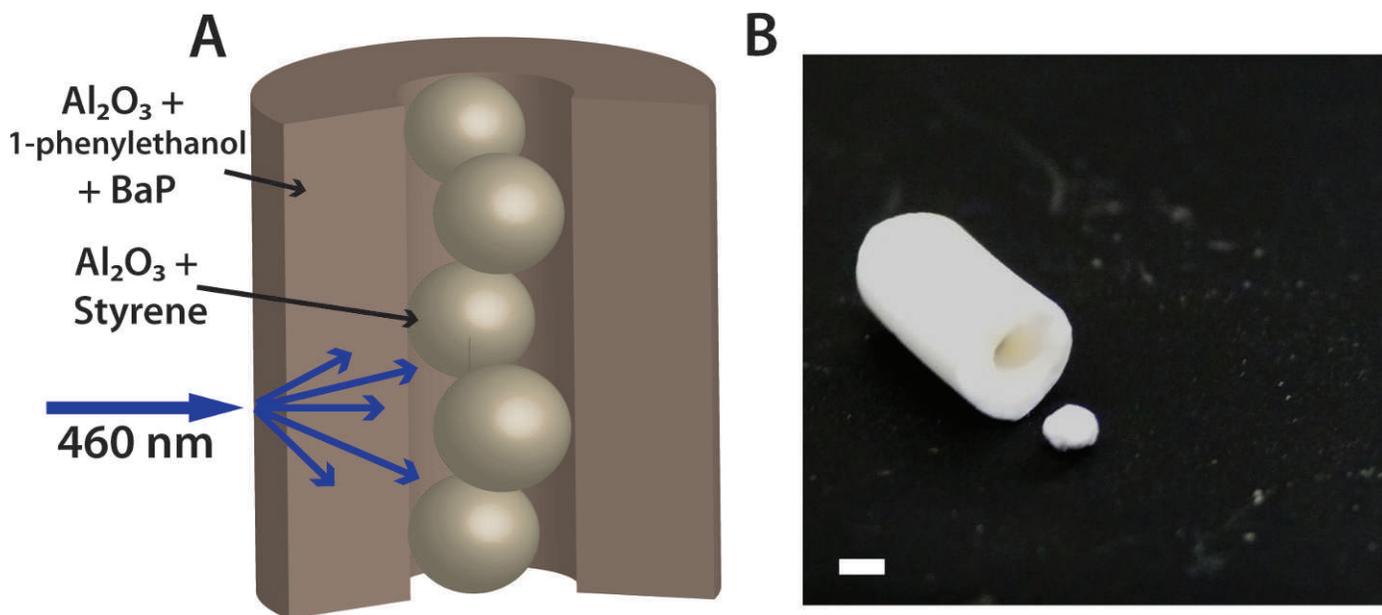


FIG. 3. (A) shows an enlarged model of the hollow Al_2O_3 pellets packed with Al_2O_3 spheres (sliced side view); and (B) is a photo of the hollow Al_2O_3 pellet and an Al_2O_3 sphere, where the scale bar in the bottom left corner is equivalent to 1 mm.

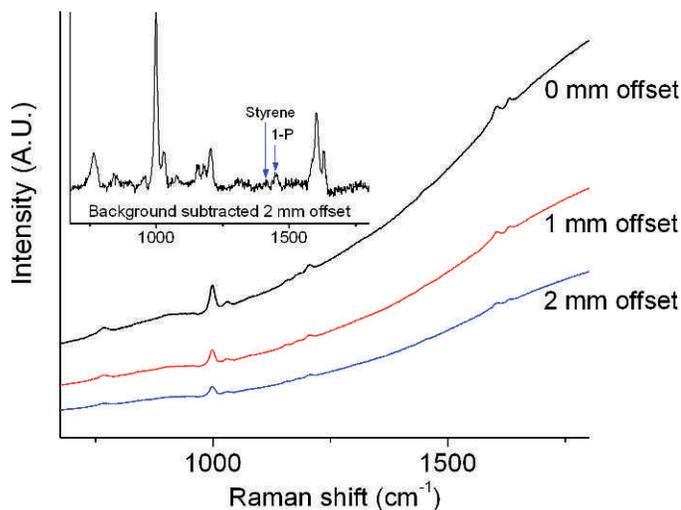


FIG. 4. CW RS and CW SORS measurements (offsets 1 and 2 mm) of model system 1: a catalytic pellet impregnated with 1-phenylethanol and BaP, with Al_2O_3 spheres impregnated with styrene. Inset shows the SORS 2 mm measurement with a background subtraction applied.

the spheres is 0.7 mm and their optical diffusivity is that of the pellet.

Model Systems. The model systems consist of combinations of an impregnated catalytic extrudate pellet and spheres (as depicted in Figure 3). Incipient wetness impregnation was carried out by contacting a certain volume of liquid with the alumina pellets or spheres by Finn pipette just sufficient to completely fill the pores of the alumina support oxide. Small alumina spheres with high porosity were used in order to improve the dispersion of the analytes, and particularly the Ag nanoparticles, in the center of the system.

In the first model system, a hollow $\gamma\text{-Al}_2\text{O}_3$ pellet is impregnated with 200 μL 1-phenylethanol (as purchased) as a first-layer marker, in addition to pretreatment with 200 μL BaP (1 μM) to provide a realistic fluorescence background, as mentioned previously. The applied laser wavelength (460 nm) excites the dried BaP aggregates, resulting in a typical broadband fluorescence background. The hollow cavity of the pellet is filled with $\gamma\text{-Al}_2\text{O}_3$ spheres that were first each impregnated with 10 μL styrene (as purchased) as a marker of the internal layer, in order to have distinct chemical signals from different layers of the sample. By illuminating the cylindrical pellet from the side, we effectively have a three-layer sample in which the first and third layer are the same (1-phenylethanol and BaP) and the core of the pellet gives a different chemical signature (styrene).

To examine the possibility of using SERS as a supporting method, a variation of this system (model system 2) is used, in which the styrene in the center is replaced by Rh6G, in the presence of SERS active Ag nanoparticles (5 μL). Ag was distributed evenly over the spheres and allowed to dry before the addition of sufficient Rh6G to completely saturate the sphere (10 μL at 10 μM , effectively reducing the analyte concentration by a factor of 10^5 compared to model sample 1).

RESULTS AND DISCUSSION

Model system 1 was characterized by CW RS, CW SORS, and TRRS, and the results are compared in Figs. 4 and 5. The CW RS measurements, summarized in Fig. 4, provide a Raman

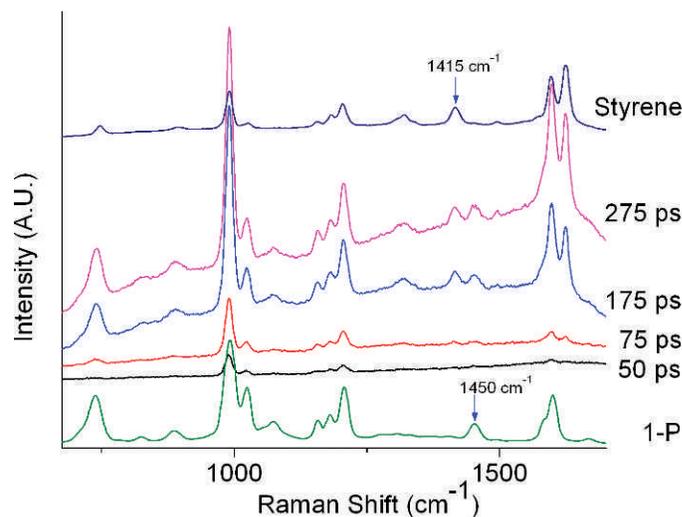


FIG. 5. Depth profiling of model system 1 by TRRS at different detector delay times. Scaled TRRS reference spectra of styrene and 1-phenylethanol (1-P) are shown at the top and bottom of the figure, respectively, and were measured for 100×500 ms. The TRRS depth profiling spectra were measured for 100×1 s.

spectrum consisting of 1-phenylethanol peaks with styrene peaks on a fluorescent background. Part of the fluorescence could have been avoided by applying long-wavelength excitation, but for this study 460 nm excitation was chosen as a worst-case scenario. In applying a spatial offset of 1 or 2 mm, the absolute intensity of the Raman signal and the fluorescence decrease to roughly the same extent (see inset for background-subtracted spectrum of the 2 mm SORS measurement).

The TRRS measurements of the same sample, shown in Fig. 5, are taken at various detector delay times and show that the 1-phenylethanol becomes visible immediately after the laser pulse. The signal is initially very low. When using a delay of 75 ps the Raman signal from styrene appears. While 1-phenylethanol and styrene share many of the strongest Raman bands (990 cm^{-1} , 1025 cm^{-1} , and 1596 cm^{-1}), differences in the spectra with increasing delay time can be seen by observing some of the weaker peaks. Most notable are a shift from 738 cm^{-1} to 748 cm^{-1} , the changing relative intensities of the bands at 1415 cm^{-1} and 1450 cm^{-1} , and the appearance of a band at 1624 cm^{-1} . Increasing the delay time results in an absolute increase in the signal of styrene with a relatively low fluorescence contribution.

The time-resolved approach is very efficient for reducing fluorescence by a factor of 20 in the Al_2O_3 extrudates under investigation, while maintaining a good signal-to-noise ratio. Side-illumination of a sample with a shell-core structure effectively transverses three layers, in which the third layer is the same as the first. Therefore, when considering the first layer signal, contributions from the third layer must also be taken into consideration. This effect, in combination with the relatively low opacity of the $\gamma\text{-Al}_2\text{O}_3$, may explain why no great advantage was found for measuring deeper layers using either technique. This results in the combination of SORS with TRRS of these catalyst bodies making no noticeable improvement in the suppression of fluorescence and a reduction in the signal-to-noise ratio due to the overall lower signal collection efficiency. Data from the combined TR-SORS measurements

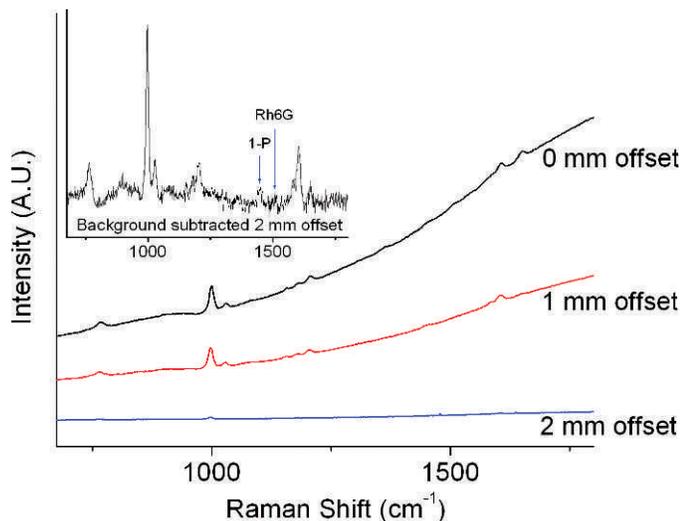


FIG. 6. CW SERS and CW SE-SORS measurements (offsets 1 and 2 mm) of model system 2: a catalytic pellet impregnated with 1-phenylethanol and BaP, with Al_2O_3 spheres impregnated with Rh6G and Ag nanoparticles. Inset shows the 2 mm offset SE-SORS measurement with a background subtraction applied.

are not shown as they confirm what was previously reported by Iping Petterson et al.²⁷

The TRRS method provides a realistic solution for fluorescence suppression in the model sample. To obtain an improved spatial resolution despite the small size and optical opacity of catalyst extrudates, TRRS can be combined with SERS to selectively enhance the core signal. The combination with SERS will also allow the study of analytes at significantly lower concentrations, as would be common in a catalytic system. This option is explored with the second model system in which styrene is replaced with Rh6G in the presence of Ag nanoparticles.

Measurements of model system 2 using CW SERS and SE-SORS are shown in Fig. 6. A mixture of Raman peaks from the first and second layers is visible on a fluorescent background. Performing background subtractions of these spectra reveals that a Raman signal from both the 1-phenylethanol in the outer layer and the Rh6G in the core of the sample can be seen.

It should be noted that the addition of SERS particles does more than enhance the Raman signal for the location where they are added. There is a potential negative effect as well: the light absorption by the SERS particles limits the number of photons that can penetrate and escape from the catalyst body, especially when they are far below the surface.³⁷ This is particularly evident in the SE-SORS measurement with 2 mm offset, which shows a significant overall signal reduction. It is clear that a balance needs to be sought between absorption and enhancement, but the availability of both Au and Ag nanoparticles for SERS, combined with excitation wavelength selection, allows some experimental design flexibility.

In Fig. 7 we explore the effect of the addition of SERS to TRRS characterization of the model system. The resulting spectra are to be compared with those obtained with CW detection (Fig. 6). In line with the data shown in Figs. 4 and 5, the results are a considerably improved fluorescence reduction for TR-SERS over the SE-SORS measurements.

These results clearly show that with similar fluorescence reduction ($\sim 10\times$) more selective analysis is possible for the core of the extrudate via the addition of Ag nanoparticles. This

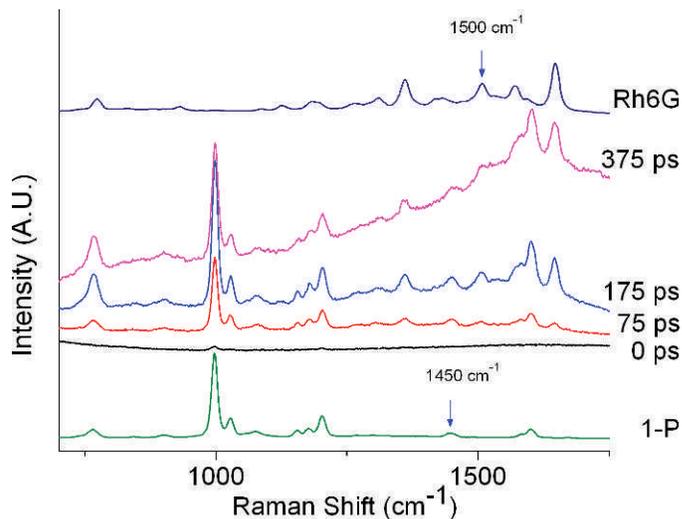


FIG. 7. Depth profiling by TR-SERS: A series of time-resolved spectra of model system 2. On the bottom of the figure is a scaled reference spectrum of 1-phenylethanol (1-P) and on the top a reference spectrum of a $10\ \mu\text{M}$ Rh6G solution in the presence of Ag nanoparticles. Spectra were measured for $50 \times 1\ \text{s}$ and reference spectra for $100 \times 500\ \text{ms}$.

is particularly promising as until now TRRS has mainly been used for detecting the major components in a sample.^{27–29} Here it is shown that, via SERS signal enhancement, realistic scenarios with lower analyte concentrations can be tackled with the same approach. Time-resolved analysis provides fluorescence reduction from the surface and bulk and can be combined with SERS enhancement to selectively enhance weaker signals at depth within catalyst extrudates.

A rough comparison of ratios of representative peaks from the shell and core of the sample shows little or no change in selectivity of signal from shell versus core with SORS (Table I). In both model systems 1 and 2 this ratio for the 2 mm SORS measurements is 2:1.

An increase in selectivity for deeper layers is generally expected with a spatially offset measurement of diffusely scattering samples. However, in this case the relative contributions from each layer remain approximately 2:1. Several factors likely contribute to this result, including the relatively low scattering properties of the impregnated catalyst body, the small diameter of the extrudate, as well as the core-shell structure of the sample.

The extrudate can be considered a three-layer system in which layers 1 and 3 are the same. Monte Carlo simulations for three-layer samples, performed by Matousek and co-workers,³⁸ showed that the ratio of the first layer to the second layer in a

TABLE I. A rough comparison of ratios of the net intensity of a representative shell peak to the net intensity of a representative core peak for both model system 1 and model system 2; background-subtracted spectra were used for these comparisons.

	Model system 1: 1450 cm^{-1} 1-P: 1415 cm^{-1} styrene	Model system 2: 1450 cm^{-1} 1-P: 1500 cm^{-1} Rho 6G
CW RS	2:1	2:1
2 mm SORS	2:1	2:1
75 ps TRRS	1:2	1:1
175 ps TRRS	1:2	1:2

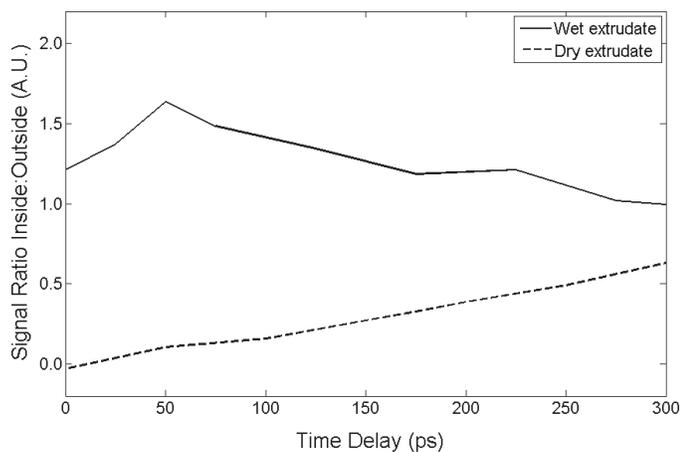


FIG. 8. Comparison of ratios of core to shell as measured by TRRS of a wet extrudate and a dry extrudate. The signal ratios change with an increasing delay time.

three-layer sample does not have a linear dependence on spatial offset in the same way that this ratio for a two-layer sample does. They found that the second-to-first-layer ratio changes very little for all offsets in a three-layer system, as the rate of decay of Raman intensity with spatial offset decreases with the depth of the layer. This is likely to also be a contributing factor to the limited selectivity for the sample core in these measurements.

With TRRS measurements the peaks for model systems 1 and 2 both have a ratio of 1:2 for 175 ps, indicating an increase in selectivity for the core of the sample in comparison to SORS, and a slight increase in selectivity with increased delay time for model system 2. The increase in signal selectivity for the inside of the sample is vital when measuring such small samples in which the desired signal may be present at very low concentration. The difference in concentration of the analytes used means that for the TR-SERS measurement the signal from the inside of the sample could be as much as 10^5 times greater compared to a situation in which SERS is not used. The effect of absorption by the SERS particles is not very detrimental to the result. The large increase in the Raman signal from the core of a catalytic extrudate when combining both TRRS and SERS will enable the detection of low concentration analytes from within real catalyst bodies in future studies. The application of SHINs in future catalytic studies will also enable the use of SERS in catalysis without chemically affecting the system under study.

It is important to keep in mind that catalyst bodies are used in gas-phase and liquid-phase reactions and that these conditions can have a significant effect on the core-shell signal ratio. In the model systems shown here the extrudate was wet with the reactant when measured, resulting in a limited depth selectivity of both the SORS and TRRS measurements due to the low optical diffusivity of the extrudate material. For dry samples the depth discrimination for both SORS and TRRS is better as the scattering of photons is more efficient and the contrast between photons from within the core to those from the shell is higher.³⁸

Observing the TRRS spectra for dry extrudates, the results with a shorter gate delay show only the outer layer, while the core is immediately visible for wet samples (Fig. 8). The gradual increase of the contribution of the core of the sample to

the spectra for dry samples continues with even longer delays, but in the wet extrudate the third layer has a greater contribution and effect on the core:shell ratio. It can be concluded that useful data can be obtained from both dry and wet extrudates, which opens up the possibility of using this technique for the study of both liquid- and gas-phase catalytic reactions.

CONCLUSION

A new approach for characterizing catalyst extrudates is found in TRRS by means of an intensified CCD camera. It overcomes one of the major problems in the practical application of Raman spectroscopy in this field—the fluorescence background from side-products and the scattering nature of the extrudate material. The short detector gate provides the advantage of overcoming fluorescent backgrounds from the sample surface as well as the bulk of the material.

The small size and core-shell nature of many extrudates complicate depth specificity of TRRS, but there is potential for 3D characterization of thicker samples. For extrudates the combination of TRRS with SERS is an option to selectively characterize a region in the material using locally applied SERS nanoparticles. The combination of time-resolution and SERS provides additional spatial selectivity within the catalytic body, but the size of this effect depends on the actual enhancement factor and the loss of signal due to light absorption. The enhancement factor strongly relates to the chemistry of the analyte and how it interacts with the SERS particles and is therefore something that needs to be evaluated for each application. The detrimental effect of absorption on signal intensity can be limited by choosing the right type and concentration of SERS nanoparticles and selecting a suitable excitation wavelength.

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