

# In-Situ UV–Visible and Raman Spectroscopy for Gas–Liquid–Solid Systems

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This paper presents the use of UV–vis and Raman spectroscopy to measure the state of a solid in a multiphase reactor. A slurry of particles and a packed bubble column were used. As this study is a proof of principle a model for an active catalyst system, insoluble pH indicators deposited on the particles and on a solid foam packing (used as the packing material in the packed bubble column) are used. This insoluble pH indicator has different UV–vis and Raman spectra according to the liquid pH. The experimental results indicate that for the slurry the spectra obtained from the moving particles can be used to characterize the state of the pH indicator. Bubbles in the packed bubble column result in disturbances in the UV–vis and Raman spectra collected from the pH indicator adsorbed to the solid surface and this interference is removed successfully with a newly developed tolerance-and-averaging method.

## Introduction

Approximately 85% of all chemical products (bulk and fine chemicals) are produced using a heterogeneous catalyst to increase the reaction rate and hence increase production capacity.<sup>1</sup> Most often the catalyst is deposited on a solid support to aid its separation from the reaction products and examples of such reactors include packed beds, fluidized beds, and slurry reactors. Multiphase reactors, where gas and liquid reactants are converted over a heterogeneous catalyst, have been used widely in the chemical industry and examples of such reactors are slurry bubble columns, trickle bed reactors, and packed bubble columns. These multiphase reactors are used in a variety of applications ranging from the production of pharmaceuticals and hydrogenations and oxidations to produce bulk chemicals (hydro-treating, desulphurization, oxidation of sulfur dioxide, etc.).

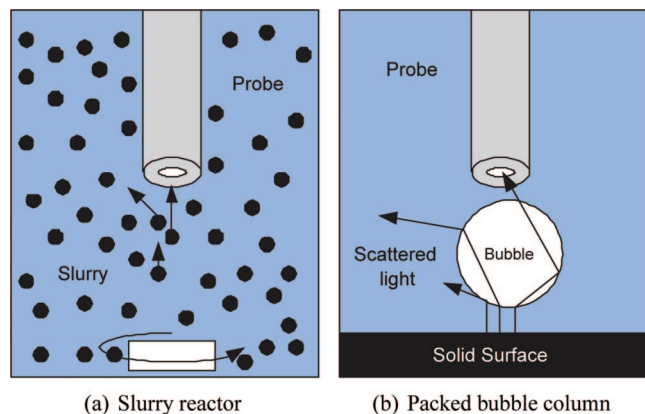
In-situ spectroscopic techniques have been developed over the years to provide much understanding into the mechanisms of catalytic reactions. In-situ spectroscopic techniques using spectroscopic probes have been applied to control gas–solid reactors operating under reaction conditions based on the state of the solid catalyst.<sup>2,3</sup> The key advantage of control based on spectroscopic information is that the actual catalytic site (catalyst state) is being probed directly, rather than the end-of-pipe response at the reactor exit. In multiphase flows an optical probe has been used to evaluate the local volume fraction of each phase in an oil–water–gas mixture,<sup>4</sup> however, spectroscopic techniques in characterizing catalysts operating in multiphase reactors (gas–liquid–solid) have not been investigated. It is the intention of this study to assess whether UV–vis and Raman spectroscopy can be used to determine the state of a solid catalyst in a multiphase reactor system. In a chemical reactor changes to a catalyst are usually slow, as good catalyst stability is very important for an industrial process. In this study we used a model system of which the state can be easily be manipulated which makes the model development more facile. Insoluble pH indicators were adsorbed on solid surfaces in a slurry of particles and in a packed bubble column. These adsorbed pH indicators are used as a model system for the catalyst in a multiphase reactor.

**In-Situ Spectroscopy.** Spectroscopic measurements (ex situ or in situ) have been widely used in the development and determination of the main parameters in the preparation affecting the stability and the size of catalytically active sites and the intrinsic reaction rate. These techniques include ultraviolet–visible spectroscopy (UV–vis), infrared spectroscopy (IR), Raman spectroscopy, X-ray absorption near edge spectroscopy (XANES), and X-ray absorption fine structure (XAFS) spectroscopy. The main techniques and their limitations in catalyst characterization are given in the books edited by Weckhuysen,<sup>1</sup> and Haw,<sup>5</sup> as well as the review papers by Weckhuysen,<sup>6</sup> and Hunger and Weitkamp.<sup>7</sup> The use of in situ spectroscopy has seen significant increase, largely due to the development of optical probes which may be used under high temperature and high pressure reaction conditions.

UV–vis and Raman spectroscopy can give quantitative information regarding the oxidation state and co-ordination of the metal oxide complexes serving as catalytically active species. The main uses of oxides of transition metals are for a number of chemical conversions such as hydrogenation, oxidation, decomposition, and isomerization.<sup>8</sup> A case study has been presented of a fixed bed where UV–vis spectroscopy (diffuse reflectance spectroscopy) and Raman spectroscopy have been used to describe changes in the Cr/Al<sub>2</sub>O<sub>3</sub> active catalyst species by increases observed in specific peaks.<sup>9</sup> These techniques have also been used to track the formation of coke to maintain an active catalyst and using this information to control the regeneration.<sup>2</sup> Combining spectroscopic techniques provides complementary quantification of the state of the catalyst and the changes occurring under reaction conditions.<sup>10</sup> However, these studies have all focused on fixed beds although the Raman spectral information from moving particles in a fluidized bed may be an attractive measure for catalysts and adsorbates to monitor and avoid the formation of coke.<sup>11</sup> An example using spectroscopy techniques to characterize the state of a slurry catalyst (Cr/SiO<sub>2</sub>) for the polymerization of ethylene, using toluene as a solvent has been illustrated.<sup>12</sup> Here the Raman spectra of toluene dominate the spectra collected from the reaction mixture and thus obscure the spectra from the catalytic active material.

UV–vis spectroscopy using visible light gives information regarding the electronic d–d and charge transfer transitions of metal oxides. It provides a convenient method to probe the state

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**Figure 1.** Schematic representation during operating conditions in (a) a slurry reactor and (b) a packed bubble column, showing the interferences at the gas–liquid and liquid–solid interfaces that scatter the light away from the optical probe.

of the active metal oxide catalyst or an adsorbed pH indicator. By the application of small optical probes, measurement is relatively easy and may also be performed through the outer wall of the reactor if made of glass.<sup>9</sup> Raman spectroscopy using laser light provides information regarding the vibrational spectra of metal oxides and organic deposits, and optical probes based on Raman spectroscopy are becoming readily available.

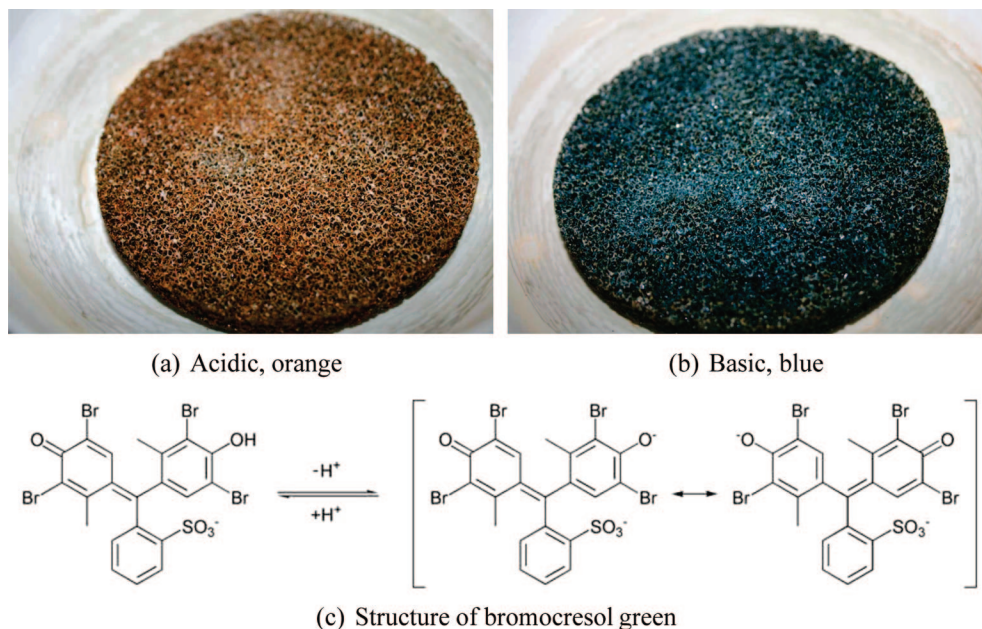
**Multiphase Reactors.** The added effect of gas–liquid and liquid–solid interfaces in gas–liquid–solid reactors contributes to the spectroscopic information collected and thus poses a challenge in obtaining reliable spectroscopic information from the catalyst deposited on the solid surface. Optical probes use optical fibers to transmit light (from a laser or lamp) into the reactor and another in the same fiber bundle to measure the reflected light (connected to a spectrometer). The interference of the liquid–solid and the gas–liquid interfaces with the light reflected from the catalyst on the solid surface is described schematically for slurry reactors and packed bubble columns in Figures 1a and 1b, respectively. These interferences need to be removed from the spectroscopic information collected to successfully determine the state of the catalyst.

**Model System.** The aim is to develop a methodology for characterization of the solid catalyst in a multiphase system. Since transitions in the state of a real catalyst are usually very slow and occur at high temperature or pressure, a model system is used as a more convenient and controllable way to demonstrate the concept. An insoluble pH indicator adsorbed on the surface of a solid support is used in this study to simulate an active catalyst to determine UV–vis and Raman spectra in multiphase systems with relative ease. The pH indicator exhibits different UV–vis and Raman spectra depending on the pH of the liquid with which it is in contact. This system thus provides a method of studying spectroscopic measurements at mild conditions (ambient temperature and pressure). The spectra collected are only from the surface of the solid particles or solid support and the contribution of the liquid to the spectra is low due to the low solubility of the pH indicator. The characteristic peaks in the UV–vis and Raman are specific to the current system. The origin of these characteristic peaks will not be discussed in detail here, since this paper focuses on the description of a methodology to do spectroscopy on a (moving) catalyst in a multiphase reactor system. The chemical origin of the bands/vibrations are less relevant and the discussion thereof is beyond the scope of this paper.

### Experimental Details

The UV–vis experiments were performed using a reflection probe consisting of a bundle of seven optical fibers (each 200  $\mu\text{m}$  thick) encased in a steel tube (120 mm in length and 6 mm in diameter). The central optical fiber is connected to a UV–vis spectrometer (AvaSpec-2048-USB2, Avantes) and the remaining six fibers are used for illumination and are connected to a light source (AvaLight-D(H)-S Deuterium-Halogen light source, 215–2000 nm, Avantes). The calibration of the reflectance spectrometer is performed using a white reference tile (WS-2, Avantes). The UV–vis spectra were recorded in LabView (LabView 7.0, National Instruments) at an integration time of 30 ms to decrease the noise to peak ratio.

The Raman experiments were performed using a reflection probe consisting of a bundle of two optical fibers (200  $\mu\text{m}$



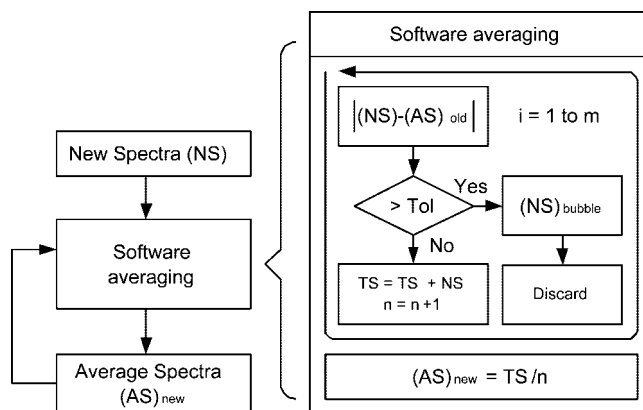
**Figure 2.** Images of a 40 ppi solid foam covered in  $\text{TiO}_2$  and insoluble pH indicator, bromocresol green, showing the acidity of the liquid medium, (a) acidic and (b) basic. (c) Structure of bromocresol green in the acidic and basic states.

connected to spectrometer and 100  $\mu\text{m}$  connected to the laser source) encased in a steel tube (76 mm in length with 12.7 mm diameter). This probe is connected to an integrated system combining a laser source (532 nm) and a Raman spectrometer (R-3000, Ocean Optics). The Raman spectra were recorded in LabView (LabView 7.0, National Instruments) at integration times between 1 and 5 s.

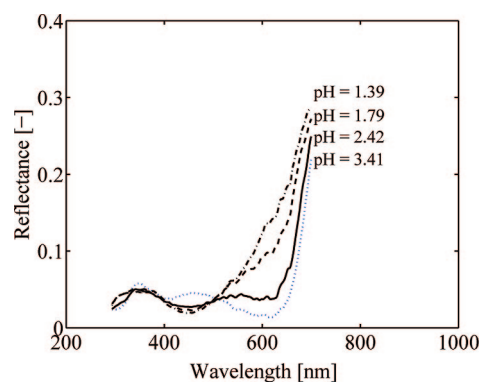
All chemicals used were laboratory grade supplied from Merck unless specified otherwise. The pH of the liquid was decreased using a solution of HCl (0.6 M) which was dosed using a titrator (TIM854, Radiometer) at a rate of 0.2–5 mL/min. The titrator also allowed measurement of the pH of the liquid using a pH-electrode (pHC2001, Radiometer). The pH indicator, bromocresol green (pH range 3.8–5.4), was dried onto the solid particles ( $\gamma\text{-Al}_2\text{O}_3$ , 63–150  $\mu\text{m}$ ) or solid foam support (40 ppi, ERG, Aerospace Corp.) from solution. This pH indicator is usually dissolved in a liquid (a mixture of water and ethanol) and exhibits different UV–vis and Raman spectra depending on the liquid pH.

**Slurry of Particles.** Alumina particles (63–150  $\mu\text{m}$ ) covered with bromocresol green were prepared using 5 wt % ethanol as a solvent and dried in an oven at 90  $^\circ\text{C}$  from solution at a liquid pH of approximately 5. The particles were filtered and washed with distilled water until the filtrate remained clear. The pH indicator has a low solubility in water and thus remains on the surface of the particles and responds in the UV–vis and Raman spectrum depending on the pH of the liquid surrounding the particles.

**Packed Bubble Column.** Aluminum foam pieces (40 ppi, ERG, Aerospace Corp.) were used as the packing material in the packed bubble column experiments. Solid foams are convenient to use due to the open structure and high surface area for deposition of the pH indicator.<sup>13</sup> The aluminum foam was dipped in a slurry of  $\text{TiO}_2$  (17 wt %, P25, Degussa) and dried while rotating at 60 rpm. Air was blown through the samples to avoid pores of the solid foam material remaining filled with the slurry. The solid foam pieces were calcined at 400  $^\circ\text{C}$  resulting in washcoats of approximately 7–10 wt %. The bromocresol green pH indicator was applied to the surface of the solid foam structure using the same preparation technique described for the slurry particles, resulting in solid foams which respond according to pH of the liquid medium, see Figure 2. The bubble column used for the experiments is a cylindrical glass vessel (diameter of 10 cm) where nitrogen is distributed through a fritted glass disk from the bottom. The solid foam was placed on the distributor and the UV–vis and Raman probes focused on the solid foam packing from the top (approximately 2–5 mm focal distance). As gas bubbles travel through the solid foam they interfere with the signal collected by the UV–vis and Raman probes. Bubble interference was removed with an in-house Labview application designed to discard compromised UV–vis and Raman spectra. This method of tolerance-and-averaging is described schematically in Figure 3. An average spectrum (AS) is created over  $m$  (e.g., 10) number of spectra. In the next cycle, the newly recorded spectrum (NS) is compared to this averaged spectrum ( $\text{AS}_{\text{old}}$ ) for the UV–vis spectra over wavelengths 300–800 nm and Raman spectra over Raman shifts 800–4300  $\text{cm}^{-1}$ . The measurement is discarded if the sum of the absolute difference between the spectra is larger than a set tolerance value. This is repeated for the next nine ( $m - 1$ ) measurements. If, for example, three spectra were discarded, a new average spectrum ( $\text{AS}_{\text{new}}$ ) is created from the remaining seven ( $n$ ) spectra and used for comparison in the next cycle. This procedure is repeated, producing a new average spectrum



**Figure 3.** Schematic representation of the tolerance-and-averaging method to remove bubble interference from UV–vis spectra. New spectra (NS) from the spectrometer are compared to an average spectrum (AS) determined over  $m$  spectra over the previous cycle. The sum of the absolute difference is compared to a tolerance value (Tol) and if larger, the spectrum is discarded. A new average is created from the  $n$  number of spectra remaining and is used in the next cycle.



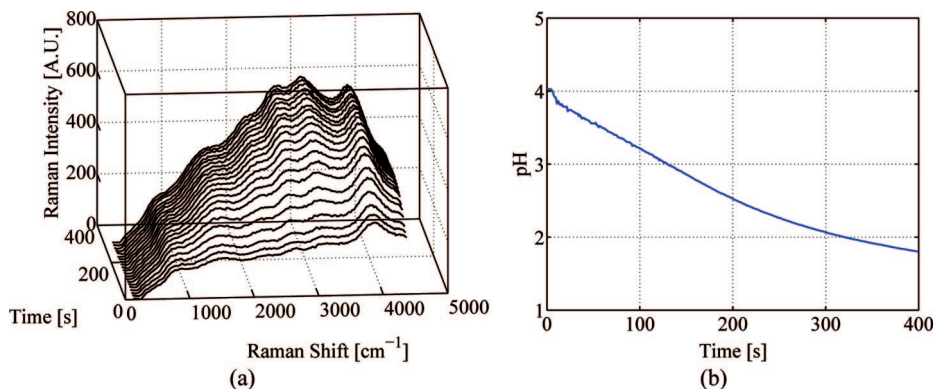
**Figure 4.** Observed UV–vis reflectance spectra for a 30% slurry of particles covered with bromocresol green, while the pH of the liquid is decreased.

for every 10 measurements. A spectrum averaged over a too large number of spectra (e.g.,  $m$  equal to 100) will have less noise, but also rapid changes in the state of the pH indicator are possibly evaluated as the interference of a bubble and thus could be lost.

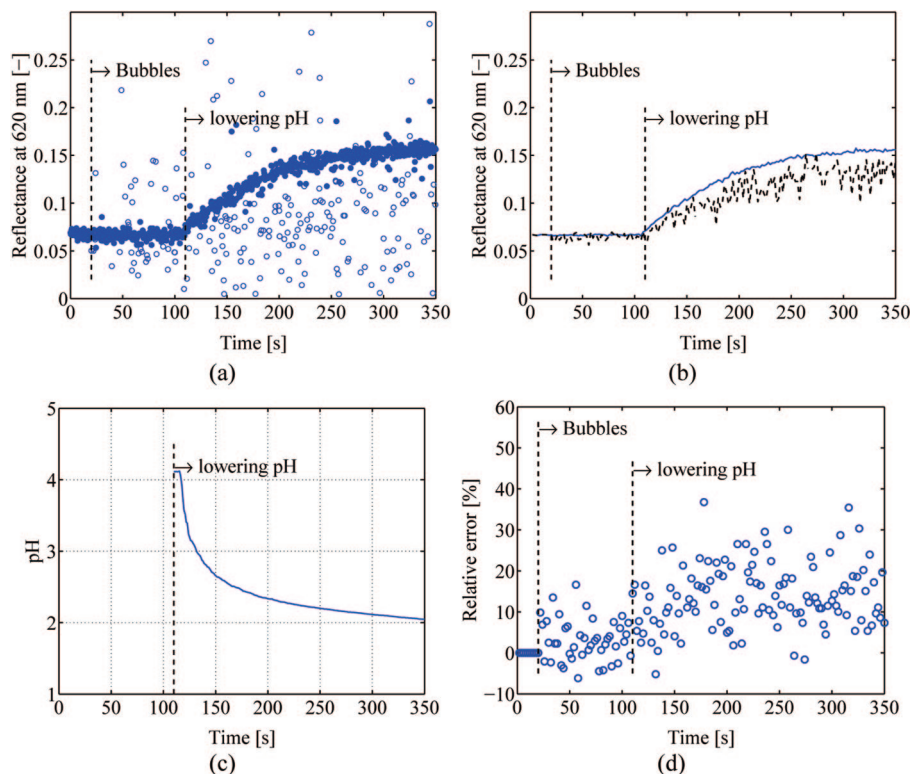
## Results and Discussion

**Slurry of Particles.** A slurry of 30 wt % alumina particles with the bromocresol green pH indicator adsorbed to the particles' surface was used to evaluate if UV–vis and Raman spectroscopy could be used to determine changes in the state of the pH indicator. UV–vis spectra were recorded every 200 ms while the pH of the liquid was decreased from 4 to 1 over a time period of 300 s. The UV–vis spectra of the slurry of bromocresol green particles are given in Figure 4 for a select number of liquid pH values. The reflectance at 620 and 450 nm increases and decreases, respectively, as the pH is decreased. Raman spectra were recorded every 15 s (integration time 5 s), while the pH of the liquid was decreased from 4 to 1 over a time period of 300 s. The Raman spectra of the slurry of bromocresol green particles are given in Figure 5. Raman intensities are observed to increase (at approximately 833, 1570, 2210, 2680, 3040, and 4000  $\text{cm}^{-1}$ ) as a result of the bromocresol green changing from the basic to the acidic state with the decrease in the liquid pH (addition of  $\text{H}^+$ ) (see Figure 2c for the structural changes). Thus, the UV–vis and Raman spectra





**Figure 5.** (a) Observed Raman spectra for a 30 wt % slurry of particles covered with bromocresol green, while the pH of the liquid is decreased over time. (b) Liquid pH-profile over time.

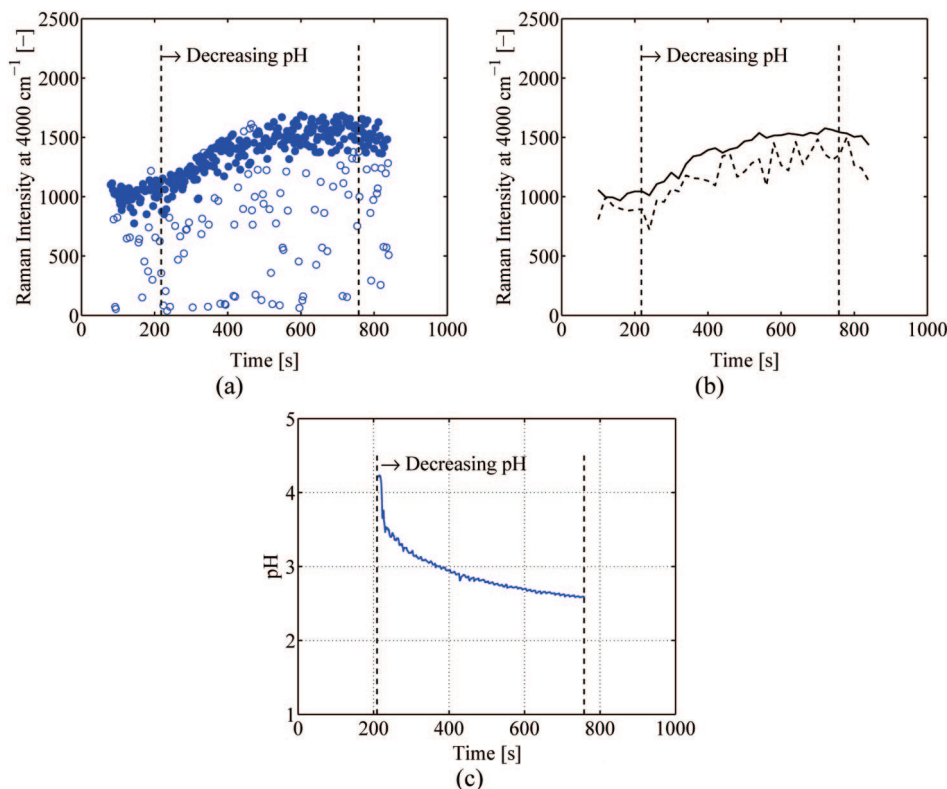


**Figure 6.** The UV-vis spectra obtained for the bromocresol green pH indicator deposited on the surface of a solid foam packing operating in a packed bubble column. (a) Reflectance at a wavelength of 620 nm is presented. The spectra which have been discarded for averaging are given by the open symbols (○) and used for determining the average in closed symbols (●). (b) The average reflectance of all data points (---) and the reflectance determined by the tolerance-and-averaging method (—) are given. (c) Liquid pH-profile over time. (d) Relative error between the average for all the data points and the average determined by the tolerance-and-averaging method.

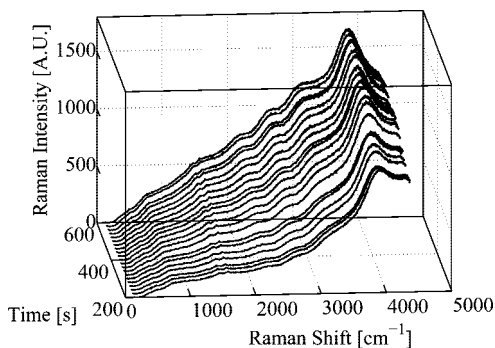
can be obtained from moving particles, and transients from one state to another can be observed.

**Packed Bubble Column.** The experiments for the UV-vis and Raman spectra resulting from the adsorbed bromocresol green pH indicator operating in a packed bubble column are shown in Figure 6–Figure 8. Fifty UV-vis spectra are recorded every 2 s and the tolerance-and-averaging method is used to assess the validity of the recorded spectra. The Raman spectra measurements are performed every 2 s and 10 are used for the tolerance-and-averaging method. In Figure 6b the average recorded UV-vis spectra for the wavelength 620 nm is given while the liquid pH is decreased, see Figure 6c. As the bubble flow starts and bubbles interfere with the UV-vis spectra and Raman spectra obtained, the tolerance-and-averaging method maintains the average spectral measurement while discarding spectra compromised by bubbles. The average UV-vis spectra

determined using the tolerance-and-averaging method shows less noise in the recorded spectra at 620 nm. The relative difference between the average reflectance determined using all the spectra and the average reflectance determined using the tolerance-and-averaging method can be as high as 30–40% (see Figure 6d). An increase in the UV-vis reflectance is observed as the liquid pH is decreased (see Figure 4). Similarly, the changing Raman intensity recorded at a Raman shift of  $4000\text{ cm}^{-1}$  as a result of decreasing liquid pH is presented in Figure 7. A figure created in a similar manner for one of the other characteristic bands visible in the Raman spectrum for the slurry particles (at approximately  $833, 1570, 2210, 2680, 3040\text{ cm}^{-1}$ ) yielded a graph with a comparable trend. The average Raman intensity increases as the pH of the liquid is decreased over time. As much as 80% of spectra may be discarded using the tolerance-and-averaging method resulting in an averaged Raman spectrum



**Figure 7.** The Raman spectra obtained for the bromocresol green pH indicator deposited on the surface of a solid foam packing operating in a packed bubble column. (a) Raman intensity at a Raman shift of  $4000\text{ cm}^{-1}$  is presented. The spectra which have been discarded for averaging are given by the open symbols ( $\circ$ ) and used for determining the average in closed symbols ( $\bullet$ ). (b) The average Raman spectra of all data points (---) and the average determined by the tolerance-and-averaging method (—) are given. (c) Liquid pH-profile over time.



**Figure 8.** The average Raman spectra obtained for bromocresol green pH indicator deposited on the surface of a solid foam packing operating in a packed bubble column as the liquid pH is decreased over time. Peaks in the Raman spectra are observed as the pH indicator undergoes transition to its acidic form.

with less noise when compared when all measurement are used. In Figure 8 the averaged Raman spectra is given for a decrease in the liquid pH over time. Comparing Figure 8 and Figure 5 shows that similar Raman intensities are observed to increase as the bromocresol green pH indicator makes a transition to its acidic form. The differences in the observed Raman spectra for the slurry of particles and packed bubble column is due the pH indicator being adsorbed onto two different materials,  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$ , respectively.

## Conclusions

UV–vis and Raman spectra recorded for a slurry of particles, and a solid foam packed bubble column are shown for insoluble pH indicators adsorbed onto the solid surface of the particles

and the solid foam packing. A change in the adsorbed pH indicator is accomplished by a change in the liquid pH and results in a clear change in the UV–vis and Raman spectra. These examples indicate that, although the UV–vis and Raman spectra are recorded under multiphase conditions, changes in the solid surface conditions can be observed. In a packed bubble column the averaging-and-tolerance method can be used to remove spectra that have been compromised by gas–liquid interfaces. The results from this study indicate that in situ UV–vis and Raman spectroscopy can be used to characterize a solid surface operating under multiphase conditions where bubbles interfere with the measured spectra.

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