Catalysis Letters Vol. 92, Nos. 3–4, February 2004 (© 2003)

Application of *in situ* surface-enhanced Raman spectroscopy (SERS) to the study of citrate oxidation on silica-supported silver nanoparticles

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Received 28 August 2003; accepted 14 November 2003

Surface-enhanced Raman spectroscopy (SERS) was used to characterize citrate anions adsorbed on nanometer-sized particles of Ag supported on SiO_2. The magnitude of the surface-enhancement effect was determined to be $\sim 3 \times 10^2$ on the as-prepared samples of Ag/SiO_2. Upon heating in air above 373 K, the citrate anions undergo oxidation to uni- and bidentate carbonate species and then decomposition to CO_2 and adsorbed O atoms. In the SERS of Ag/SiO_2, a very strong enhancement of the $\nu(C=O)$ signal for the bidentate CO_3 species was observed for temperatures between 398 and 448 K, which is accompanied by an increase in the UV–vis absorbance of the sample at the frequency of the laser line used for Raman spectroscopy. This phenomenon is attributed to an increase in the surface-enhancement effect caused by clustering of the Ag nanoparticles as they sinter at elevated temperatures. The present investigation shows that the proper interpretation of *in situ* SERS spectra requires an understanding of the changes occurring in the UV–vis spectrum of the sample.

KEY WORDS: SERS; silver; citrate oxidation.

1. Introduction

Raman spectroscopy can provide complementary information to infrared spectroscopy in studies of adsorbed species present on the surface of supported metal catalysts. This is particularly true in the region below 1500 cm^{-1}, where many supports strongly absorb infrared radiation making it difficult, if not impossible, to obtain useful spectra. The principal limitation of Raman spectroscopy is that the amount of scattered light is only a small fraction ($\sim 10^{-6}$) of the incident light, which makes it difficult to observe low adsorbate coverages or adsorbates with small scattering cross sections. A dramatic increase in the intensity of the Raman signal can be achieved when molecules are adsorbed on roughened metal surfaces and the frequency of the incident light is close to that of the phonon resonance [1]. This phenomenon, known as surface-enhanced Raman scattering (SERS), has been used widely to study the adsorption state of reaction substrates on electrodes and their electrochemical reactions in aqueous media [2]. On the other hand, the use of SERS to study gas-phase reactions occurring on solid surfaces has been quite limited. The dehydroamination of alcohols [3], the reductive coupling of benzoic acid derivatives [4] and epoxidation of ethylene [5] are the only examples of the use of SERS for such purpose; however, no proof for SERS is provided in these studies nor is the magnitude of the SERS enhancement factor reported.

The SERS effect has been observed for various metals, but principally coinage and alkali metals. Of these metals, silver exhibits a very large enhancement factor over a wide range of excitation wavelengths. Since silver is an active catalyst for a number of important reactions, such as ethylene epoxidation [6], methanol oxidative dehydrogenation [7], NO reduction [8] and the selective reduction of α,β-unsaturated aldehydes [9], the use of SERS to investigate the structure of adsorbed species on silver is quite relevant. This communication illustrates the application of SERS to the oxidation of citrate anions on the surface of Ag particles supported on SiO_2. The magnitude of the SERS enhancement factor is evaluated and the relationship between the magnitude of this factor and the optical adsorption of the catalyst at the wavelength of the laser used to obtain the Raman spectra is discussed. The results show that the magnitude of the SERS signal is affected by the size of the Ag particles and the extent to which they cluster.

2. Experimental

Silica-supported silver was prepared by dispersing 5 g of SiO_2 (Sigma, fumed silica, mean diameter = 7 nm)

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1011-372X/04/0200–0093/0

into 250 mL of an aqueous solution of $AgNO_3$ (8.95×10^{-4} to 3.65×10^{-2}M). After the suspension had been refluxed for 1 h, 50 mL of sodium citrate (SC) solution (1.39×10^{-4} to 5.64×10^{-3}M) was added dropwise with vigorous stirring; the molar ratio of $AgNO_3$/SC in all preparations was fixed at 1.6. During this step, the color of the suspension changed from milky-white to greenish-brown owing to the deposition of Ag. Reflux was continued for an additional hour in order to complete the Ag reduction. The resulting product was vacuum filtered and redispersed into 200 mL of distilled water. This filtration/redispersion process was repeated three times to assure the removal of any soluble silver salt. Finally, the Ag/SiO_2 product was dried in flowing air overnight to remove excess water. If necessary, the particles were also dried under vacuum at room temperature. A sample containing x-wt% Ag is designated as $Ag(x)/SiO_2$.

A reference sample was prepared in the same way as $Ag(16.4)/SiO_2$ except that $AgNO_3$ was not added to the water used to suspend the silica. The amounts of citrate and partially oxidized citrate remaining on the samples after washing (abbreviated as citrate below) in the reference and $Ag(16.4)/SiO_2$ were determined by elemental analysis to be 3.19 and 3.41 wt% respectively.

Raman spectra were recorded using a HoloLab series 5000 Raman spectrometer (Kaiser Optical) equipped with an Nd:YAG laser that is frequency-doubled to 532 nm. The laser was operated at a power level of 25 mW measured at the sample with a power meter (Edmund Scientific). A TEA/CCD detector (Princeton Instruments) was operated at −40 °C. Spectra were recorded with a resolution of $1\,cm^{-1}$. Approximately 50 mg of Ag/SiO_2 was pressed into a wafer at 5000 psi and placed onto a sample holder within a quartz Raman cell. The samples were rotated at 400 rpm during the measurements to reduce the effects of sample heating by the laser. During the temperature ramp, a gas flow of $50\,cm^3\,min^{-1}$ of zero grade air (Matheson) was passed over the catalyst pellet. Temperature-programmed oxidation (TPO) was performed in a quartz microreactor using 200 mg of Ag/SiO_2. A gas flow of $60\,cm^3\,min^{-1}$ of 10% O_2 in He (Scott Specialty Gases) was passed through the sample and the exiting gas was monitored using a UTI 100C mass spectrometer. The temperature in the reactor was ramped at a rate of $10\,K\,min^{-1}$ from room temperature to 773 K and held for 1 h to ensure that all organic species were removed from the sample.

3. Results and discussion

Figure 1 shows the UV–vis spectra of $Ag(x)/SiO_2$: A, $x = 4.83$; B, $x = 16.4$. The as-prepared samples exhibit relatively sharp absorption bands at 309 ± 2 and 366 ± 1 nm. These bands can be assigned to the

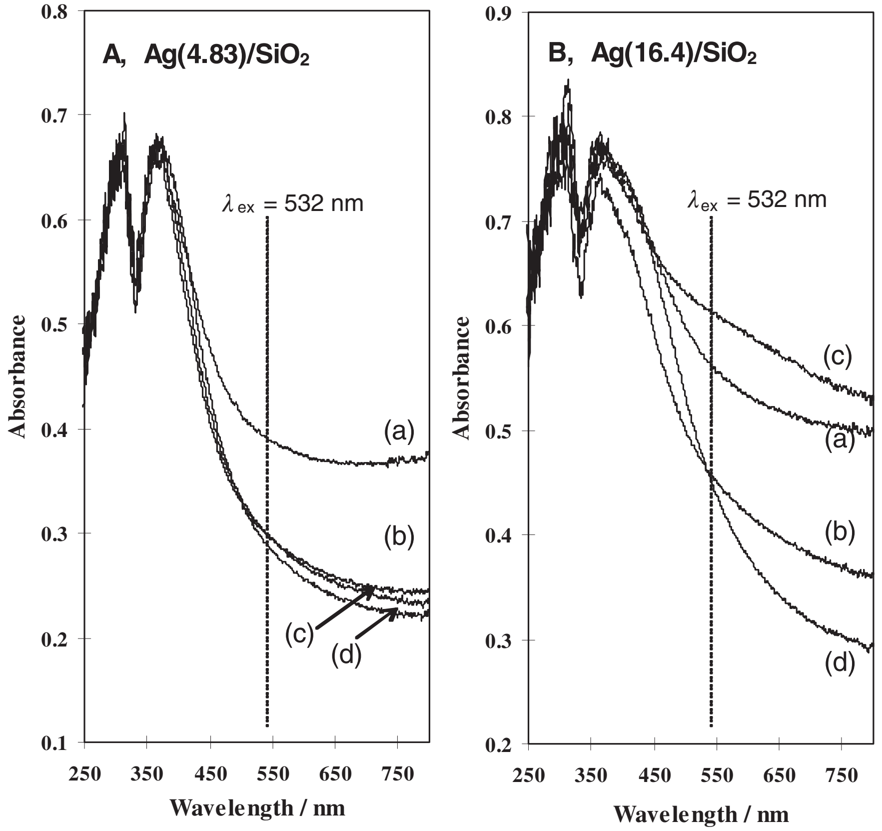

Figure 1. Electronic absorption spectra of $Ag(4.83)/SiO_2$ and $Ag(16.4)/SiO_2$: (i) as prepared; (ii) 373 K; (iii) 423 K; (iv) 473 K.

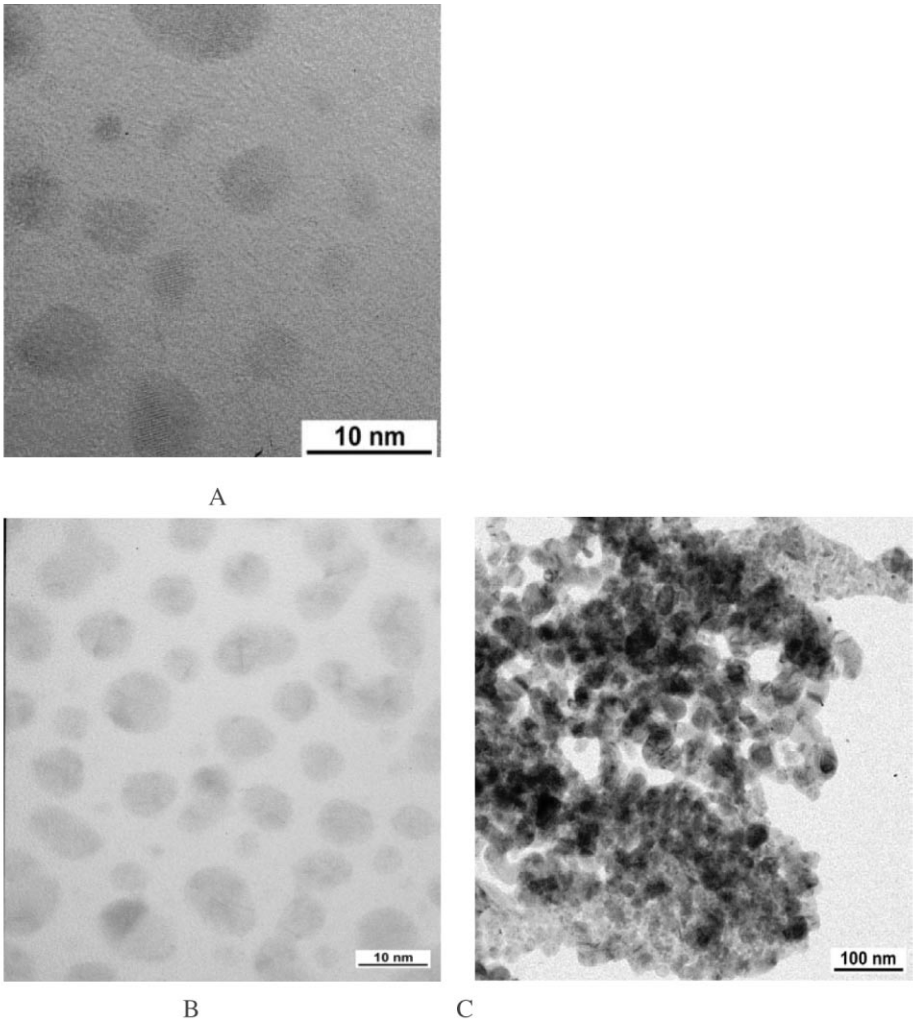

Figure 2. TEM Images of Ag/SiO2 samples: (a) Ag(4.8)/SiO_2 as prepared; (b) Ag(16.4)/SiO_2 as prepared; (c) Ag(16.4)/SiO_2 heated at 423 K.

electronic transitions of Ag^+ cations and the surface plasmon band of silver nanoparticles, respectively[10]. Silver cations are most likely present as SiO^--Ag^+ formed by cation exchange of Si-OH groups present on the surface of silica. The full width at half-maximum (FWHM) of the surface plasmon band of Ag particles can be related to the mean diameter of the particles (d) by the equation $d = v_f/\Delta\omega_{1/2}$, where v_f is the Fermi velocity of the free electron in silver and $\Delta\omega_{1/2}$ is the FWHM of the surface plasmon band in angular frequency [11]. The mean value of d for the as-grown Ag/SiO_2 samples was estimated to be 2.1 ± 0.4 nm for $0.48 \leq x \leq 16.4$ wt%. Figure 2(a) and (b) show representative TEM images of the 4.8 wt% and 16.4 wt% samples of Ag/SiO_2. The average particle size determined from these images is consistent with that determined from figure 1 and does not vary significantly with Ag loading.

Figure 3 shows Raman spectra of as-prepared Ag(x)/SiO_2 samples with varying amounts of Ag: $0 \leq x \leq 16.4$ wt%. No signal was observed in the spectrum of the reference, whereas the spectrum of Ag(16.4)/SiO_2 has well-defined bands at 2939, 1550, 1392 and 933 cm^{-1}, which are assignable to $\nu_{as}(CH_2)$, $\nu_{as}(COO)$, $\nu_s(COO)$ and ν(C-C) respectively (table 1). The inset in figure 3 shows that the intensity of the most intense $\nu_s(COO)$ signal is proportional to the value of x and can be expressed as $I(x) = 1050x + 58.59$. The uncertainty of the base line is responsible for the fairly large error observed for larger values of x. The results presented in figure 3 demonstrate that the observed Raman signal is ascribable to citrate anions adsorbed on Ag and that the citrate anions on SiO_2 are not observable. Since the molar ratio of citrate/$AgNO_3$ was fixed in the preparation of Ag/SiO_2 and the diameter of the dispersed Ag particles is almost independent of x, the linearity of $I(x)$ indicates that the surface density of citrate anions adsorbed on the surface of the Ag particles is nearly constant. The signal positions for citrate anions in an aqueous solution are also listed in table 1. Each citrate band appearing in figure 3 is redshifted by 24–33 cm^{-1} relative to the corresponding band for citrate anions in aqueous solution. The redshift of the Raman bands for the

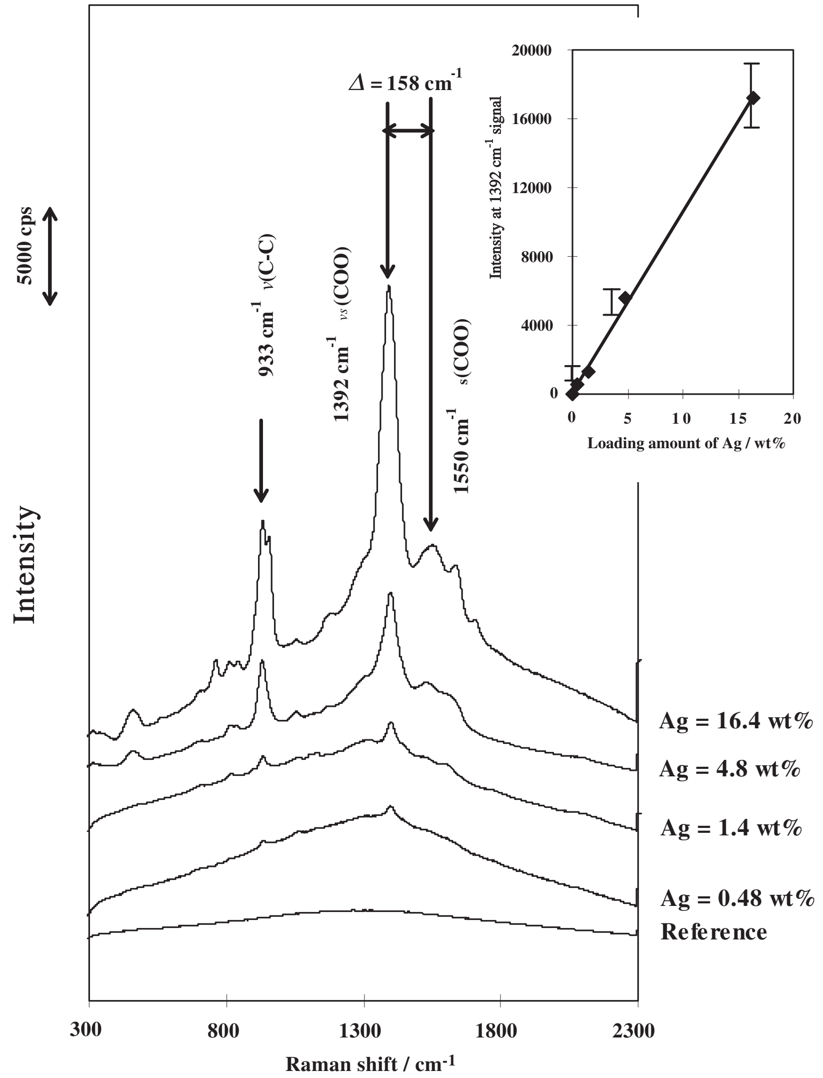

Figure 3. Raman spectra of as-prepared Ag/SiO$_2$ samples with different Ag-loading amounts. The inset shows the relation between the ν_s(COO) signal intensity and the loading amount of Ag.

adsorbed citrate anions is similar to that reported for the citrate anions adsorbed on colloidal Ag [12]. The split between the signal positions of ν_s(COO) and ν_{as}(COO) (Δ) is sensitive to the mode of surface coordination of the carboxylate group [13]. A value of $\Delta = 158\,\mathrm{cm}^{-1}$ indicates that the carboxylate groups of citrate anions form a bidentate structure. The intensity of the ν_s(COO) band in the spectrum of Ag(16.4)/SiO$_2$ containing 3.41 wt% citrate is $17\ 300 \pm 2000$ cps. As a standard, the Raman spectra of physical mixtures of sodium citrate (y wt%) and SiO$_2$ particles were acquired for $0 \leq y \leq 47.7$ under the same conditions as those used for Ag/SiO$_2$. The most intense ν_s(COO) signal intensity at $1394\,\mathrm{cm}^{-1}$ is almost proportional to the value of y: $I(y) = 21.65y - 16.88$. The surface-enhancement factor is calculated from the ratio of the scattering intensity for Ag(16.4)/SiO$_2$ to that for a physical mixture of sodium citrate and SiO$_2$ with the same citrate content, 3.41 wt%. Thus, a surface-enhancement factor of $\sim 3 \times 10^2$ is obtained from the ratio $I(x = 16.4)/I(y = 3.41)$. The magnitude of the observed SERS enhancement factor is identical to that reported for phthalocyanine adsorbed on hemispheroidal particles of Ag having an average diameter of 70 nm and an average height of 40 nm when the wavelength of the exciting laser light is 514.5 nm [14]. The enhancement factor of 3×10^2 is smaller than that reported for Ag colloidal systems [12], which could be due to the higher laser wavelength used in this experiment and the fact that the silver particles are supported on silica.

Figure 4(a) and (b) show *in situ* Raman spectra of Ag(4.8)/SiO$_2$ and Ag(16.4)/SiO$_2$ taken while the catalyst was heated in air. Less than a 2% decrease in the intensity of the ν_s(COO) band was observed because of laser heating prior to the onset of heating in air. Figure 4(a) shows that the intensity of the bands

Table 1
SERS data of citrate adsorbed on Ag/SiO_2 in air

Frequency (cm^{-1})			Assignment
298 K	398 K	523 K	
2939	–	–	$\nu_{as}(CH_2)$
1635	–	–	$\delta(H_2O)$
	~1590[a] (1590–1630)[b]	–	ν (C=O, bi-CO_3)
	1546 (1470–1530)[b]	–	ν_a(OCO, uni-CO_3)
1550 (1580)[c]	–	–	ν_{as}(COO)
1392 (1418)[c]	–	–	ν_s(COO)
	369 (1360–1373)[d]	–	ν_s(OCO, uni-CO_3)
	1265 (1260–1288)[d]	–	ν_a(OCO, bi-CO_3)
933 (957)[c]	–	–	ν (C-C)
~813 (846)[c]	–	–	ν (C_4-O)
	656 (663–683)[d]	–	δ_a (COO, bi-CO_3)
464 (463)[e]	446	340–500	ν(Ag-O(subsurface))
320 (325)[f]	–	340–500	ν(Ag-O(ads))

[a] Very strong shoulder.
[b] Reference [15].
[c] Measured for a 0.34 M aqueous solution of sodium citrate.
[d] Reference [16].
[e] Reference [17].
[f] Reference [18].

for adsorbed citrate anions present on Ag(4.8)/SiO2 diminishes as the temperature is increased from 298 to 323 K. Raising the temperature to 348 K results in the complete loss of the citrate bands and the appearance of weak features at 1546, 1369, 1265 and 656 cm^{-1}, all of which are attributable to carbonate species (table 1) [15,16]. These bands become more prominent as the temperature is raised and reach a maximum intensity at 423 K. The signals observed at ca. 1590 cm^{-1} (strong shoulder) and 1546 cm^{-1} are assignable to the C = O stretching vibrational mode of CO_3 adsorbed on Ag particles via bidentate coordination (ν(C = O, bi-CO_3)) and the OCO antisymmetric vibrational mode of CO_3 adsorbed on Ag particles via unidentate coordination (ν_a(OCO, uni-CO_3)) respectively. In addition, broad bands centered around 1369 and 1265 cm^{-1} are observed, which can be attributed to ν_s(OCO, uni-CO_3) and ν_a(OCO, bi-CO_3) respectively. These observations indicate that above 373 K, citrate anions are oxidized on the surface of the Ag particles to yield both uni- and bidentate carbonate species. Disappearance of the carbonate bands above 423 K is attributed to carbonate decomposition. This interpretation is supported by TPO spectra for Ag(16.4)/SiO_2, which show that the decomposition of adsorbed carbonate species to form CO_2 and adsorbed O occurs rapidly at $438K \leq T \leq 525K$. Taken together, these observations suggest that O atoms adsorbed on the surface of Ag particles are responsible for the oxidation of citrate anions. Evidence for subsurface and adsorbed O atoms is provided by the weak bands observed at 464 cm^{-1} and 320 cm^{-1}, respectively. These features have been reported previously on Ag and are known to contribute to the oxidation of adsorbed organic species [17,18]. A weak band in this region, characteristic of silver oxides, has also been attributed to the Ag-O stretch of adsorbed oxygen species [19].

The series of spectra shown in figure 4(b) for Ag(16.4)/SiO_2 is very similar to that shown in figure 4(a), the principal difference being the manner in which the peak intensities change with temperature, particularly between 398 and 448 K. The extent of growth in the intensity of the carbonate bands with increasing temperature is much larger than that observed in figure 4(a) for Ag(4.8)/SiO_2. This difference can be associated with differences in the changes in the UV–vis spectrum of the two samples, which occur with increasing temperature. Figure 1(a) shows that for Ag(4.8)/SiO_2 the absorbance in the region of the laser line (532 nm) decreases monotonically with increasing temperature upon heating in air, whereas in the case of Ag(16.4)/SiO_2, the absorbance at 532 nm first decreases, then increases and finally decreases again as the temperature is raised from 298 to 473 K. The decreases in UV–vis absorbance can be ascribed to sintering of the Ag particles and the consequent growth in particle size. This change has been found to cause a loss in the SERS enhancement factor [20]. The increase and subsequent decrease in UV–vis intensity seen in figure 1(b) for Ag(16.4)/SiO_2, occurring between 373 and 473 K, is probably due to clustering of the Ag particles as they sinter. As seen in figure 2, the TEM image of this sample after heating to 423 K clearly shows evidence for both sintering of Ag particles and formation of particle

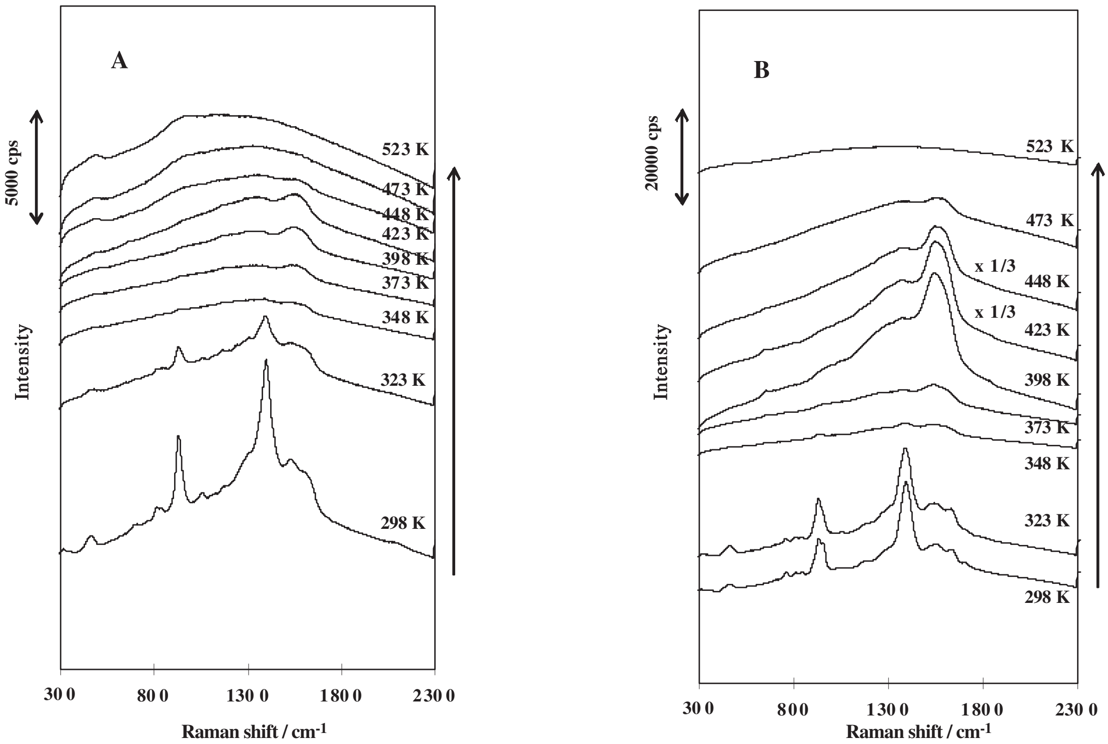

Figure 4. *In situ* SERS of Ag/SiO_2 with heating: (a) $Ag(4.8)/SiO_2$; (b) $Ag(16.4)/SiO_2$.

clusters. Studies conducted with colloidal suspension of both Ag and Au particles have shown that clustering causes an increase in the optical absorbance of the suspension and an increase in the intensity of the Raman signal for adsorbed pyridine that is nearly proportional to the square of the optical absorbance. This effect of clustering can be attributed to dipolar interactions between particles [21,22]. Theoretical calculations show that as the particles in a two-dimensional array are brought closer and closer together, the SERS enhancement factor first increases and then decreases [20]. Thus, we suggest that the unusually large increase in the intensity of the carbonate bands observed during the oxidation of adsorbed citrate anions on $Ag(16.4)/SiO_2$ is due to the formation of arrays of Ag particles.

The present study has quantified the magnitude of the SERS effect for citrate anions adsorbed on 2-nm diameter Ag particles supported on SiO_2. The strength of the SERS enhancement factor is strongly related to the optical absorbance of the sample at the laser frequency. For a fixed Ag-weight loading, growth in the size of the Ag particles causes a decrease in the magnitude of the SERS enhancement factor. This decrease can be strongly offset by the formation of particle clusters. The dipolar interactions arising from such structures can increase the observed SERS enhancement effect. Consequently, the interpretation of *in situ* SERS spectra requires an understanding of the changes occurring in the UV–vis spectrum of the sample. Failure to realize this could lead to misinterpretation of observed Raman spectra.

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