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A Surface-Enhanced Raman Study of Ethylene and Oxygen Interacting with Supported Silver Catalysts

PETER H. MCBREEN[1] AND MARTIN MOSKOVITS

University of Toronto, Department of Chemistry, Toronto M5S 1A1, Canada

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Surface-enhanced Raman spectroscopy was used to study two silver-based catalysts following exposure to C_2H_4/O_2 mixtures at different temperatures. The catalysts were formed in one of two ways. In the first, aqueous silver colloid was filtered through a silica glass fiber filter. In the second, silver metal was electrochemically deposited in the pores of anodic aluminum oxide. Spectral features due to amorphous carbon were detected at 1370 and 1596 cm^{-1}. Samples heated in ethylene-rich mixtures displayed the carbon peaks up to a temperature of 455 K beyond which the carbon features were essentially absent. A spectral feature was observed at 995 cm^{-1}. This and another weaker spectral feature at 676 cm^{-1}, which was seen only in the spectrum of the sample below 400 K, showed a frequency shift upon using $^{18}O_2$ and were therefore assigned to vibrations involving oxygen. Tentatively they were ascribed to O_2^- and O_2^{2-} moieties.

INTRODUCTION

Raman spectra obtained from molecules adsorbed on specially prepared silver samples have been found to be up to several million times more intense than expected for an equivalent number of molecules in solution or the gas phase. This phenomenon, dubbed surface-enhanced Raman scattering (SERS), has been reviewed widely (*1*).

Silver films formed by deposition onto a cold (100–150 K) substrate have been found to be SERS active, while silver films deposited upon substrates held at room temperature are SERS inactive. In a previous paper (*2*) we reported ellipsometic data which showed that the optical properties of the two types of silver film are markedly different. The cold-deposited film was found to be strongly absorbing in the region 350–600 nm as compared with the room temperature deposited film. We were able to simulate the observed difference by modeling the cold-deposited film as a silver layer covered with spherical bumps forming a "roughness layer." The origin of the SERS effect is related to the optical properties of the rough surface (*3*). As suggested previously (*4*) the surface roughness layer may be considered as a two-dimensional collection of metal particles. With this in mind we wish to see if SERS could be applied to a three-dimensional aggregate of metal particles such as a dispersed metal catalyst. Supported silver particle catalysts are unique for the reaction of ethylene with oxygen to yield ethylene oxide, it is, therefore, a logical choice to use SERS to study the interaction of C_2H_4 and O_2 with supported silver particles. We are aware of three other studies with the same aim. Pockrand and Otto (*5*) studied oxygen adsorbed on silver; likewise Wood (*6*) reported preliminary data in this area. More recently Weaver and co-workers (*7*) used SERS to look at ethylene oxidation on sputtered Ag foils with and without chlorine treatment.

EXPERIMENTAL

The experiments were performed using two different types of supported silver samples. The two types differed in the nature of the support and in the manner of prepara-

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[1] Present address: CRAM, Université Laval, Quebec G1K 7P4, Canada.

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tion. For this reason we do not differentiate them as Ag on Al_2O_3 and Ag on SiO_2, but rather as type A and type B samples.

Type A samples were prepared by a novel technique (*8*) which enables the electrodeposition of metals into the porous aluminum oxide layer of an anodized aluminum foil. The anodizing process produces a porous film where the pore size is determined by the anodizing voltage and the type and concentration of electrolyte. In the present case the pores were approximately 300 Å in diameter. The alumina surface layer, formed in the anodizing process, behaves as a rectifier thus enabling the electrodeposition of silver using an alternating voltage. The metal is deposited in the form of small particles as shown by Goad and Moskovits (*9*), but these are too small to be seen with SEM. The deposited silver is found to be primarily inside the pores.

Type B samples were prepared by filtering silver colloid solution through Whatman glass fiber filter paper. Orange colored colloidal suspensions were repeatedly filtered until the filter paper became very dark. Then the sample was left to dry in air prior to reduction in H_2 at high temperature. Representative SEM pictures of type B samples are given under Results.

Two experimental arrangements for heating the samples were employed. In one arrangement the samples were mounted on a resistive heater which was sealed in a glass reaction chamber. The glass reaction chamber was constructed large enough so that Raman emissions from the glass walls would not be collected simultaneously with those from the catalyst. Even so, a thorough analysis of the Raman spectrum of glass was performed in order to assure ourselves that none of the Raman spectral features studied originated from that source. The heater contained a tungsten wire spring element which was encased in Macor machinable ceramic and coated with Dylon refractory cement and in turn with Saureisen porcelain. The samples were pressed against the heater by silver wire.

Temperature measurement were made using a Chromel–Alumel thermocouple pressed tightly against the heater assembly. This experimental arrangement allowed for *in situ* studies at high sample temperature. In the second arrangement heating was achieved by placing a glass tube containing the samples in a cylindrical oven. This arrangement obviated interference due to the presence of hot filaments, but it restricted spectral measurements to 300°C.

Raman spectra were recorded using a SPEX Model 1400 double monochromator equipped with photon counting and interfaced to a Tektronix 4052 computer. Emissions were excited by means of an Ar^+ laser.

RESULTS

The results shown in Figs. 1–3 were obtained using a Type A sample mounted on the resistive heater. The sample was reduced *in situ* by repeated heating to 675 K in fresh charges of 1 atm of hydrogen. Between some of the initial charges of hydrogen the sample was exposed to air in order to facilitate the removal of surface carbon.

Figure 1a shows that the Raman spectrum of the reduced sample, at 300 K, displays intense bands at 1370 and 1596 cm^{-1}. These bands are associated with surface carbon (*10*) and are referred to in this section as the carbon bands. As Fig. 1b shows, no change in the Raman spectrum was observed when the reduced sample was subsequently exposed to 400 Torr O_2 at room temperature. The sample was then heated to 775 K and recooled to 550 K. At 550 K, as shown in Fig. 1c, no Raman bands were observed. However, on cooling to 300 K a broad feature centered at approximately 750 cm^{-1} emerged (Fig. 1d), but the carbon bands did not reappear. The sample was then evacuated of oxygen and exposed to a static pressure of 1 atm C_2H_4 at 300 K. Figure 2a shows that the exposure to ethylene leads to the reappearance of the carbon bands in addition to the feature at 750 cm^{-1}. When the temperature of the sample

FIG. 1. SERS spectra obtained after the interaction of 400 Torr O_2 with a reduced type A sample. (a) The reduced sample at 300 K, (b) the reduced sample under 400 Torr oxygen at 300 K, (c) spectrum recorded at 550 K following the interaction of oxygen with the sample at 775 K, and (d) spectrum obtained on subsequently cooling the sample in oxygen to 300 K. All spectra were recorded with 514.5-nm Ar$^+$ laser excitation.

was raised to 550 K, in the presence of C_2H_4, all Raman bands were removed (Fig. 2b). The sample was then heated to 750 K and recooled to 450 K whereupon the carbon bands were observed again. Figure 2c shows that the latter heat treatment caused a marked sharpening of the carbon band at 1590 cm^{-1}, and the formation of a broad band at 830 cm^{-1}. The sample was then evacuated of C_2H_4 (Fig. 3a) and exposed to a static pressure of 250 Torr O_2 at 300 K. The latter exposure caused no significant change in the SERS spectrum. Figure 3b shows that when the sample temperature was raised to 465 K in 250 Torr O_2 only the carbon bands were observed. On raising the sample temperature further to 550 K all the Raman bands were removed (Fig. 3c). The sample was subsequently cooled to 300 K in the oxygen ambient and spectrum 3(d), which displays weak carbon bands and a broad band at 770 cm^{-1}, was obtained.

The series of spectra displayed in Fig. 4 were obtained using a type B sample mounted on the resistive heater. The reduced sample displayed intense carbon

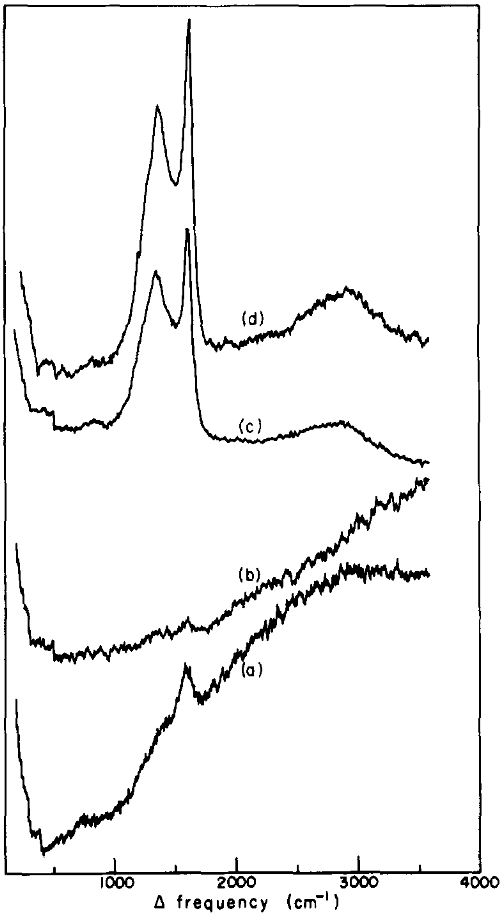

FIG. 2. SERS spectra obtained for the interaction of 1 atm C_2H_4 with the oxygen treated (Fig. 1) type A sample. The oxidized sample (a) on addition of C_2H_4 at 300 K, (b) on subsequently heating to 550 K, (c) on subsequently heating to 750 K and recooling to 450 K, and (d) on subsequently cooling to 300 K under the C_2H_4 atmosphere.

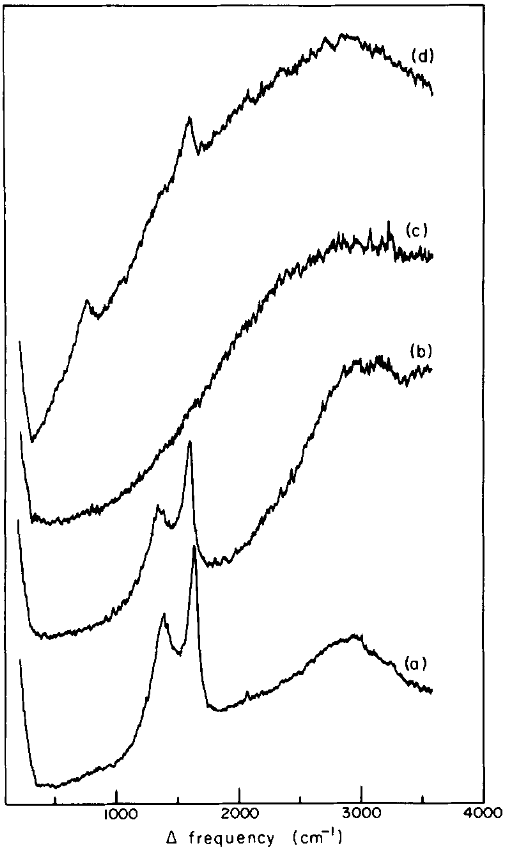

FIG. 3. The above spectra were obtained on evacuating the sample giving rise to spectrum 2(d), and adding 250 Torr O_2 at 300 K. The sample under O_2 (a) at 300 K, (b) at 465 K, (c) at 550 K, and (d) subsequently at 300 K.

bands, a weak band at 671 cm^{-1}, and two very weak bands at 240 and 1000 cm^{-1}. The latter two bands appeared as poorly resolved shoulders on the Rayleigh emission and carbon peaks, respectively. When a 400 Torr C_2H_4/O_2 mixture, in the pressure ratio 94 : 6, was added to the reduced sample at 300 K (Fig. 4a), no change in the spectrum was observed. The sample temperature was then raised to 350 K (Fig. 4b), and after approximately 200 min at 350 K in the gas mixture the band at 995 cm^{-1} became clearly resolved (Fig. 4c). This change occurred at the expense of the carbon peaks. When the sample temperature was raised to 410 K (Fig. 4d) the latter changes became more pronounced. The rate of change increased when the sample was heated to 465 K (Fig. 4e), and when the sample was subsequently maintained at 455 K for 200 min spectrum 4(g) was obtained. In this spectrum the carbon bands are almost completely removed and the band at 995 cm^{-1} is apparently quite intense. However, a comparison of spectrum 4(c) with spectrum 4(g) shows that the latter band has approximately the same absolute intensity in both cases. That is, the peak is simply revealed by the removal of the carbon peaks. The peak at 670 cm^{-1} is clearly visible in spectra

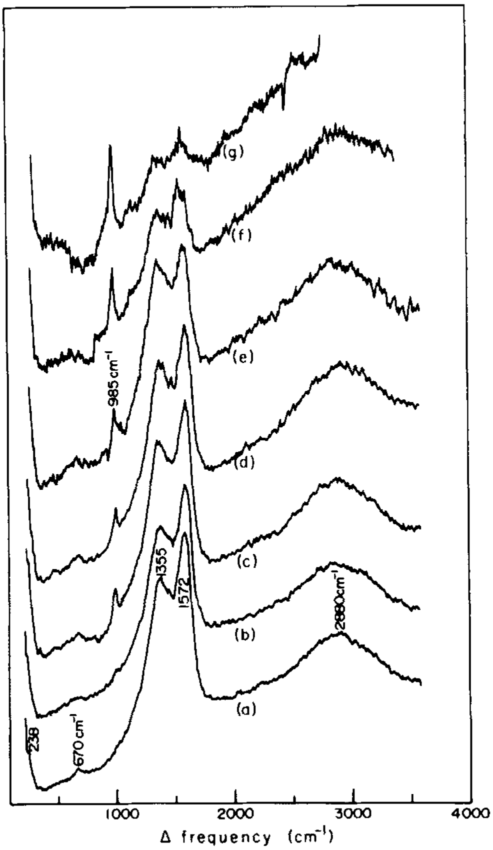

FIG. 4. SERS obtained with 488-nm Ar$^+$ laser excitation for a type B sample in the presence of a 600 Torr C_2H_4/O_2 94 : 6 mixture. The reduced sample under the gas mixture (a) at 300 K, (b) at 350 K, (c) after 200 min at 350 K, (d) at 410 K, (e) at 465 K, (f) subsequently at 455 K, and (g) after 200 min at 455 K. The amplification factors used in recording spectra (a) to (g) are (a) 1, (b) 1.07, (c) 1.6, (d) 1.6, (e) 3.4, (f) 4.0, and (g) 4.21.

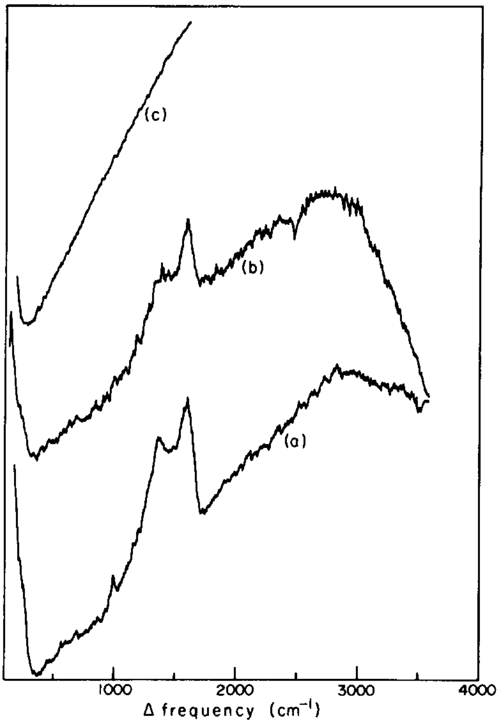

FIG. 5. Spectrum (a) was obtained subsequent to spectrum 4(g) on cooling the type B sample in the C_2H_4/O_2 gas mixture to 300 K. Spectra (b) and (c) were obtained for a silver impregnated anodized aluminum foil (type A sample) and a silver-free anodized aluminum foil, respectively, which were subjected to the same conditions as the sample giving rise to spectrum (a). Laser line: 488 nm.

4(a) to 4(f). The band giving rise to the shoulder at 240 cm^{-1} appears to increase in intensity in the sequence 4(a) to 4(f). As shown in Fig. 5a the carbon bands returned when the sample was recooled to 300 K in the gas mixture.

In the above experiment a type A sample and a strip of anodized aluminum, in addition to the type B sample for which spectra 4(a–g) and 5(a) were recorded, were mounted on the resistive heater. The three samples were therefore subjected to identical treatments. Spectra 5(b) and 5(c) were recorded subsequent to spectrum 5(a) with the samples at 300 K. One can see that the simple anodized aluminum sample yields no enhanced Raman signal, whereas the silver impregnated sample displays the carbon bands.

The spectra shown in Fig. 6 were obtained using type B samples. In this series of experiments two pieces of silver impregnated glass filter papers were mounted inside a glass tube. Heating was achieved using a cylindrical oven, and the Raman spectra were recorded as 300 K. The experimental arrangement was such that there existed a 100 K temperature gradient between the two samples. Apart from this difference in temperature the pretreatment and exposure of both samples was identical. Thus sample 1 was reduced in 600 Torr hydrogen at 625 K, and sample 2 at 725 K. Both reduced samples displayed the two intense carbon peaks and a broad CH stretching band. Both samples were then exposed to 52 Torr $^{18}O_2$ at 300 K. On heating sample 2 further to 560 K the carbon bands were

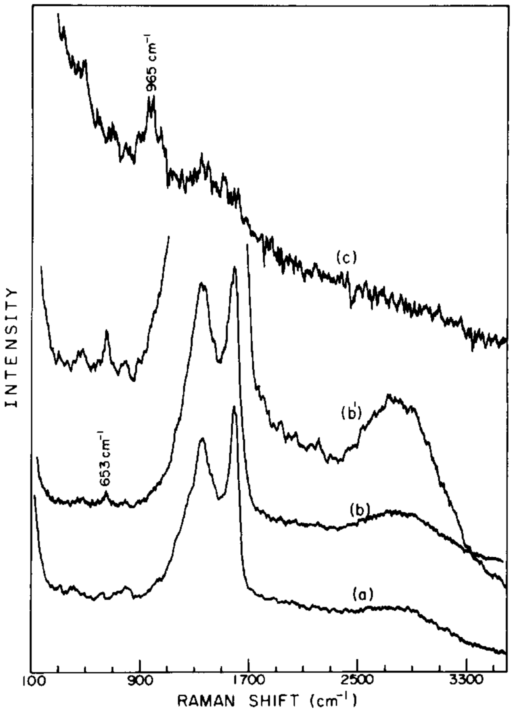

FIG. 6. SERS spectra obtained following the interaction of $^{18}O_2$ with a reduced type B sample at (a) 300 K, (b) 480 K, and (c) 560 K. The spectra were all recorded at 300 K. Laser line: 514.5 nm.

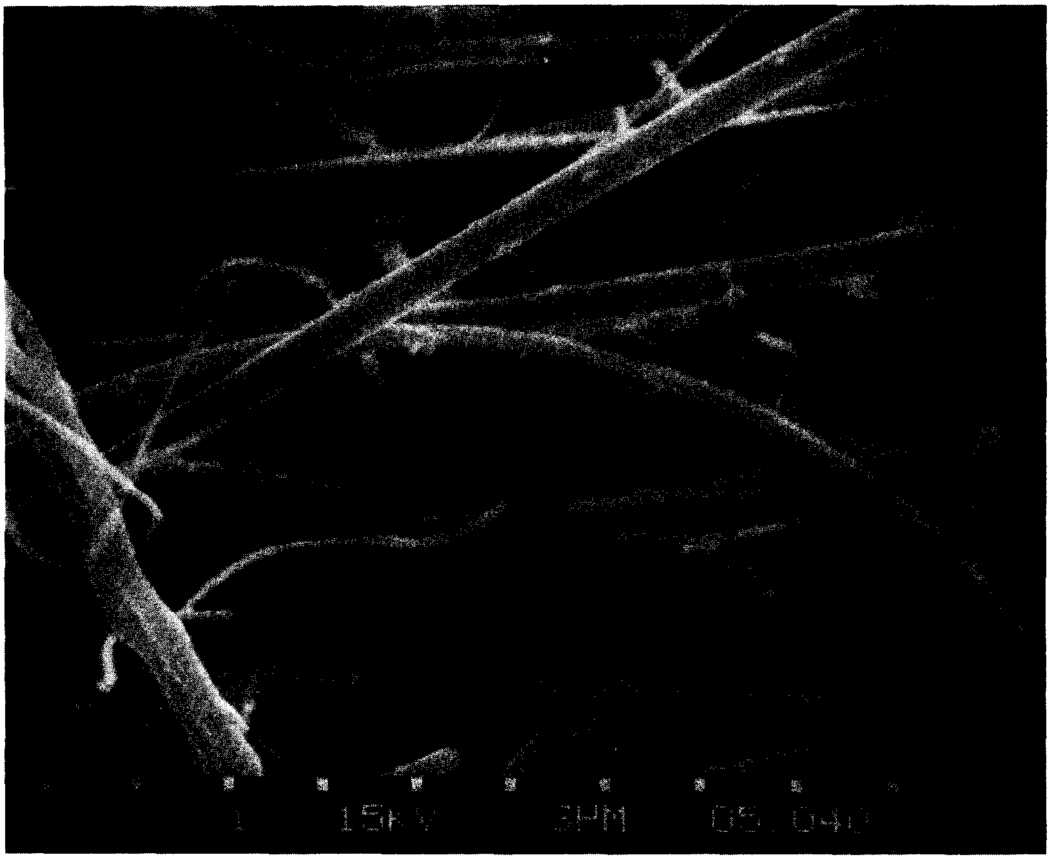

FIG. 7. Scanning electron micrograph of the glass fibers of a Whatman glass fiber filter.

markedly decreased in intensity, and a band at 965 cm^{-1} appeared (Fig. 6c).

The surface structure of the catalysts used may be gauged from the scanning electron photographs shown in Figs. 7 through 10. Figure 7 shows the glass fibers of the Whatman glass fiber filter before impregnation with silver. Figure 8 shows the surface following impregnation but before H_2 reduction Fig. 9 shows the surface after Ag impregnation and following reduction in H_2 at 350°C. Figure 10 shows the anodic oxide structure of the type A catalysts. The silver particles are contained within the pores and are too small to be detected by SEM.

In our experiments, both 488- and 514-nm laser excitation gave more or less equally intense (and almost identical spectra). The 457-nm excitation produced significantly less intensity for excitation with a beam of the same power. This implies a decrease in SERS intensity for this sample in the violet. The 610-nm R6G radiation produced a Raman spectrum of somewhat lower enhancement than that obtained with 514 nm implying that the peak enhancement for our samples lay somewhere near the yellow or orange region of the spectrum.

Careful temperature monitoring showed also that illumination with the laser did not produce a significant warming of the catalyst samples, nor was there evidence for a significant photochemical contribution to the formation of products.

DISCUSSION

In terms of SERS per se the striking result of these experiments is that under ap-

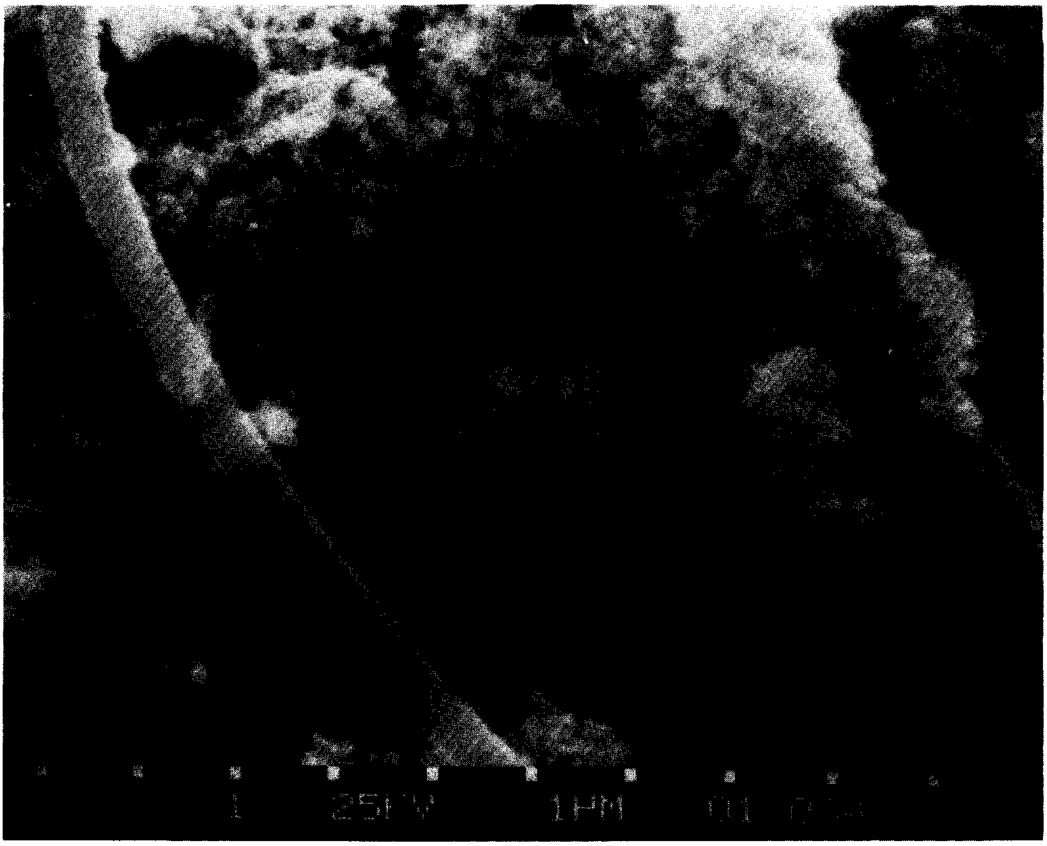

FIG. 8. As in Fig. 7 but following impregnation with colloidal silver particles and before H_2 treatment.

propriate conditions the technique may be used to study silver samples at high temperatures. Type B samples which were reduced in H_2 at 725 K displayed surface Raman enhancement (Fig. 4). Similarly, from Fig. 1 one can see that heating a type A sample to 770 K in 400 Torr O_2 did not quench the SERS activity. The commercial production of ethylene oxide is carried out in the 520–600 K range using silver particles supported on low surface area refractory materials (*11, 12*). Thus SERS may be a feasible technique for the study of the epoxidation reaction *in situ*.

The observed SERS signal is due to the presence of silver particles on the supports. This is confirmed by comparing the Raman spectra of silver-free and silver impregnated samples. For example, in Fig. 5 the SERS spectrum obtained with a sample of anodic alumina (c) is compared with that of a silver impregnated sample (b). The latter sample yields a SERS spectrum, the former does not.

The SEM photographs show that immediately upon filtration the silver deposits on the type B catalysts consist of "fluffy" masses of metal consisting of very small particles with a mean dimension smaller than 200 Å. After hydrogen treatment at 320°C there occurs a fair amount of sintering. In Fig. 9, for example, one sees silver particles as large as 1000 Å while before H_2 reduction particles of that size were absent. Nevertheless the bulk of the silver particles remain in the less than 1000 Å size range.

There exists a well established connection between silver sample morphology and

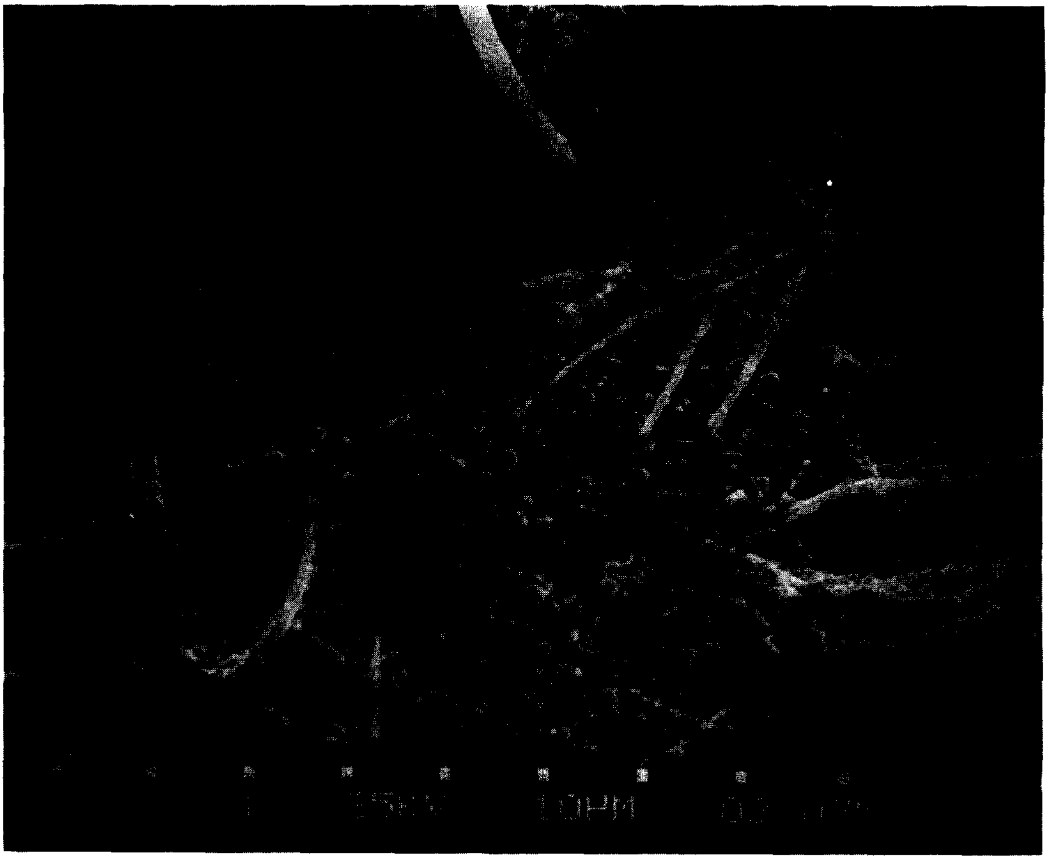

FIG. 9. As in Fig. 8 but following H_2 reduction at 623 K.

SERS activity (*3*). SERS is best observed with rather small, interacting particles. With some types of samples there is a loss in SERS activity (*13*) due to sintering. In type A and type B samples, however, the support minimizes the sintering of the silver particles.

We now concentrate on the behavior of carbon on the silver particles as revealed by the SERS spectra. The observed intense carbon bands at 1370 and 1590 cm^{-1} are commonly observed in SERS experiments. Using SERS and EELS Tsang *et al.* (*10*) have identified the features as belonging to amorphous (α) carbon. They observed the bands even in cases where the α-carbon coverage was below the level detectable by Auger electron spectroscopy ($<10\%$) of a monolayer). Tsang *et al.* (*10*) accounted for the intensity of the features in terms of a combination between the surface Raman enhancement and the large intrinsic cross section for Raman scattering of the carbon. The authors noted that the high frequency band correlates with the Raman spectrum of crystalline graphite, and that the second band arises through the relaxation of the Raman selection rules in the case of the disordered α-carbon. This fact was recognized earlier in the work of Tuinstra and Koenig (*14*) who showed that the band at around 1355 cm^{-1} occurs only in disordered graphite. Its intensity was found indeed to correlate with the size of the carbon particle: the smaller the particle the greater the ratio of the 1355-cm^{-1} band to the one at 1575 cm^{-1}. This observation was reiterated more recently by Johnson and Thomas (*15*) in a

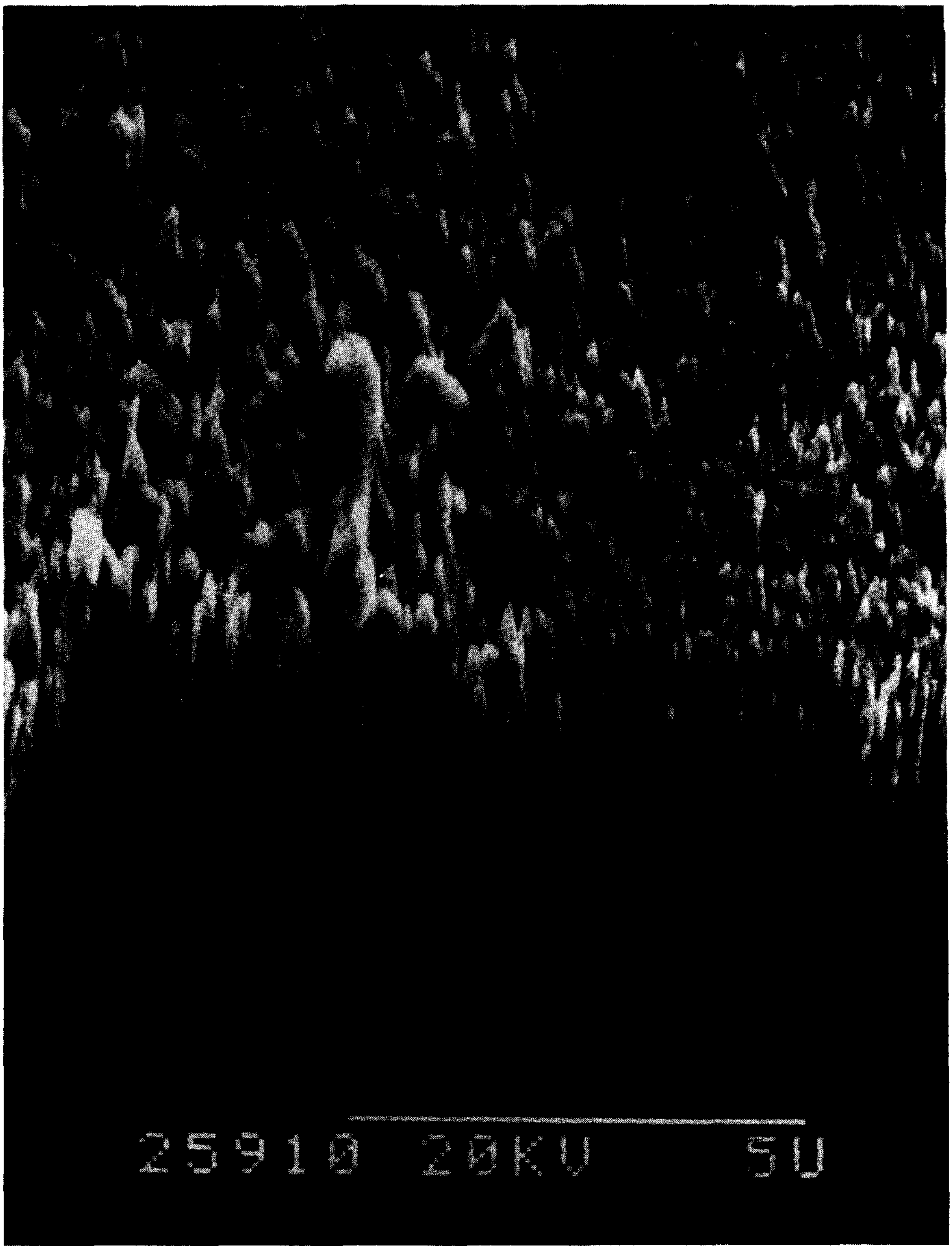

FIG. 10. Scanning electron micrograph of the anodic oxide structure of the type A catalysts.

study of carbon deposits. The breadth of these bands was also found to correlate with carbon particle size (*14*). Although it might be dangerous to extrapolate the quantitative findings of those authors to our carbon films it is clear both from the intensity of the 1355-cm^{-1} band and the bandwidths we observe that we are dealing with a very thin carbon layer indeed, one perhaps no more than a monolayer thick.

Our SERS spectra show that the surface carbon on the supported silver is to some extent hydrogenated. A very broad (520 cm^{-1} FWHM) CH stretching band was found to accompany the carbon bands. Experiments with carbon layers derived from exposure to C_2D_4 produced and isotope-shifted a broad CD band indicating that the band results from C—D stretching and that its carrier originates at least in part from the C_2D_4 exposure. The qualification, however, results from the fact that the maximum in the isotope-shifted band occurred at a higher frequency than expected for a normal C—D bond indicating that one or more of the following is taking place: (i) the H does not occur in a simple C—H bond but may be bridging two C atoms or perhaps is interstitial, (ii) that part of the very broad CH manifold is, in fact, an overtone of the carbon bands, which, of course, would not isotope-shift (indeed the CD band was found to be broader than the CH band), or (iii) that some residual C_2H_2 or hydrogen in some other form was present in the system or (perhaps subcutaneously) in the sample, yielding some CH contribution to the CD band. Although all three explanations are possible we prefer the last.

The degree of H or D incorporation into the carbonaceous surface layer was also found to vary from sample to sample and with temperature as suggested by the variability of the intensity of the CH band to the carbon peaks. The width of the CH band was also found to be variable suggesting, perhaps, a variety of H binding sites upon the carbon deposit.

All of the freshly reduced samples displayed the intense α-carbon Raman bands. In the 450–550 K temperature range these bands disappeared even for a sample held under 1 atm of C_2H_4 (Fig. 2b). For the latter sample the full intensity of the carbon bands was restored on recooling the sample to 450 K (Fig. 2c). However, heat treatment to 750 K, with the sample under 1 atm of C_2H_4, caused a marked sharpening of the high frequency carbon band. This change is attributed to ordering of the surface carbon due to increased mobility at high temperature. The width of the mode at approximately 1590 cm^{-1} is particularly sensitive to long range order of the carbon (*10*).

It is possible, however, that the observed changes arise through interaction of the carbon with oxygen. The sample for which the spectra shown in Fig. 2 were recorded had been previously exposed to 400 Torr O_2 at 775 K, and therefore probably contained some dissolved oxygen. Backx *et al.* (*16*) report that for Ag(110) samples subsurface oxygen is in equilibrium with surface atomic oxygen at 470 K. However, considering the surface science results obtained by a number of groups it is also possible that the disappearance in the carbon Raman bands in the 450–550 K region arises from a transformation in the nature of the surface carbon itself. This is the interpretation given by Madix (*17*) for the disappearance of the LEED pattern obtained with C_2 adsorbed on Ag(110) upon heating to 550 K. According to his interpretation the C_2 species cleave to give carbidic C atoms in registry with the underlying substrate. (The C_2 species resulted from the decomposition of acetylene on oxygen pretreated Ag(110) leading to C_2H and C_2 upon heating, respectively, to 170 and 275 K.) The formation of carbonaceous layers as a result of the interaction of other hydrocarbons with atomic oxygen adsorbed on Ag(110) is also known (*18–20*). A low coverage of C_2 species, on the other hand, is sufficient to block oxygen adsorption. In light of these results a possible cause of the disappearance of the carbon bands upon heating our sample to 450–550 K is the transformation of α-carbon to adsorbed carbon atoms. Alternatively reaction with subsurface oxygen may be responsible for the observation. Although the former explanation seems attractive in light of its similarity to what was previously observed on Ag(110), it is difficult to reconcile it with the further observation that the α-carbon bands return upon cooling the sample and vanish anew upon heating it. One would expect the surface to saturated eventually with carbon atoms halting the process. Nevertheless the current results are in good qualitative agreement with UHV studies of well defined Ag(110) samples; and SERS has the added capability for studying silver samples under high pressure conditions.

Several groups have shown that the probability for the reaction of ethylene with adsorbed oxygen on silver is extremely small (*16, 12, 20, 19*). Furthermore, it is very difficult, though not impossible (*22*), to achieve a detectable population of molecular oxygen on silver at 300 K under UHV conditions. Thus in the case of the epoxidation reaction the ability of SERS to monitor the surface processes *in situ* is very important.

It is desirable to have information concerning oxygen species on silver since there exists a correlation between the relative concentration of surface oxygen species and the product distribution in the epoxidation reaction (*21, 25, 26*). In the present set of experiments no Raman peaks which could be unambiguously assigned to adsorbed atomic oxygen were observed. In EELS experiments a loss at 312 cm^{-1} is observed for atomic oxygen on Ag(110) (*16*). The present SERS experiment did however yield Raman bands which may possibly be associated with adsorbed molecular oxygen. Eickmans *et al.* (*23*) in a SERS study of oxygen adsorbed on cold-deposited silver films observed peaks at 497 and 1053 cm^{-1} which they attributed to peroxidic (O_2^{2-}) and superoxidic (O_2^-) species, respectively. The peaks centered at 676 and 995 cm^{-1} in spectra 4(a)–(g) and 5(a) may possibly arise from the same two species, the anomalously low stretching frequency of 614 cm^{-1} for molecular oxygen on Ag(110), as observed using EELS, is usually interpreted in terms of metal electron transfer to an oxygen π^* orbital. This interpretation is supported by UPS data (*24*). Thus for such a heterogeneous surface, in terms of structure and chemical composition, as that of a supported silver particle it is reasonable to expect considerable variations in the O_2 stretching frequency. Further support for the presence of adsorbed molecular oxygen is given by the results obtained using $^{18}O_2$. Figure 6 shows that the interaction of $^{18}O_2$ with type B samples leads to a band at 655 cm^{-1} (spectrum 6(b)) and another at 960 cm^{-1} (spectrum 6(c)) on heating to 480 and 560 K, respectively. If one were to interpret the 676- and 995-cm^{-1} bands as arising from O—O stretching, then converting $^{16}O_2$ to $^{18}O_2$ should yield isotope-shifted frequencies of 637 and 938 cm^{-1}, respectively. The observed frequencies (655 and 960 cm^{-1}) may be understood if one assumes the presence of sufficient quantities of subsurface $^{16}O_2$ to cause the predominant surface species in the $^{18}O_2$ experiment to be of the $^{16}O^{18}O$ variety. This leads to expected frequencies of 656 and 966 cm^{-1}, respectively, in good agreement with what is observed. Other options (for example, that the 995-cm^{-1} bands is due to a C—O vibration) lead to less satisfying agreement. Likewise the possibility that the observed bands originate from the enhancement of silica support vibrations seems unlikely but not entirely inconceivable. Silica is known to have a vibrational band at approximately 1100 cm^{-1}.

If our assignment is correct then the results imply that molecular oxygen can exist on the surface of silver under conditions approaching those for epoxidation catalysis.

The shoulder at 240 cm^{-1} which is partly resolved in the spectra shown in Fig. 4 may possibly be due to a carbon-metal stretching vibration or to a molecular oxygen–metal vibration. However, we present this assignment as highly speculative. In EELS spectra of molecular oxygen on Ag(110) the oxygen metal vibration is observed at 240 cm^{-1} (*16*).

Moreover we will not make too much out of the observed progress of the 676- and 995-cm^{-1} bands and the α-carbon bands with heating (Fig. 4). Upon introducing the O_2/C_2H_4 mixture to the catalyst both the

676-cm^{-1} band and the α-carbon bonds grew in. The 676-cm^{-1} band disappears on heating, while the 995-cm^{-1} band grows in and remains prominent when all the carbon is gone. Since we do not know if the various bands observed proceed from species in close contact or displaced from one another upon the surface we cannot comment with confidence upon the apparent suggestion of the above observation that it is the peroxidic O_2 which seems to be the more reactive species toward the O_2/C_2H_4 feed.

In addition to the bands which we have attributed to carbon and adsorbed ions of molecular oxygen we observed weak, broad bands in the range 700–900 cm^{-1} (for example, Fig. 2c). Because of their low intensity neither a precise frequency nor a precise interpretation will be given. It is, however, noteworthy that they appear with catalysts which were found to produce largely gas phase CO_2. Since carbon dioxide is known to interact with oxygenated silver surfaces to produce surface carbonate (*16*) we suggest that these bands may be due to adsorbed carbonate.

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