In Situ High Temperature SERS Study of Ag Catalysts and Electrodes during Ethylene Epoxidation

INTRODUCTION

In situ spectroscopic investigation of adsorbed reactants, products, and intermediates on catalyst surfaces under pressure and temperature conditions of practical importance has been a long-sought goal in heterogeneous catalysis. It has been well established that adsorption of molecules on rough metal surfaces causes a dramatic enhancement of Raman scattering intensities (*1, 2*). This phenomenon (SERS) has already been used extensively to study the state of adsorbed species on metal electrodes in aqueous solutions (*3–5*). SERS has also been used to study metal catalyst surfaces. Considerable attention has been focused on Ag surfaces exposed to O_2 and/or ethylene due to the industrial importance of the Ag-catalyzed ethylene epoxidation. Previous SERS studies of O_2 (*6, 7*) and C_2H_4 (*8, 9*) adsorption on Ag surfaces were limited to UHV and cryogenic temperature conditions. In a more recent study SER spectra were obtained at temperatures as high as 550 K with supported Ag catalysts exposed to C_2H_4/O_2 mixtures (*10*).

In this work, *in situ* SER spectra were obtained at atmospheric pressure and temperatures 300–700 K on a porous polycrystalline Ag catalyst film, which could also be used as an electrode in a stabilized ZrO_2 solid electrolyte cell. The catalytic properties of the Ag film were studied in the same cell by gas chromatographic and mass spectroscopic analyses of reactants and products. The aims of the investigation were (i) to examine *in situ* the state of adsorbed species during reaction over the entire temperature range of practical importance for

C_2H_4 epoxidation and (ii) to examine the effect of electrochemical O^{2-} pumping through the solid electrolyte on the SER spectra, since O^{2-} pumping has been found to induce dramatic and reversible changes on catalytic activity (*11*).

EXPERIMENTAL

The cell reactor setup used to obtain *in situ* high temperature SER spectra of Ag catalysts exposed to a steady flow of C_2H_4, O_2 and N_2 at atmospheric pressure is shown in Fig. 1. The porous Ag catalyst film had a superficial surface area of 2 cm^2 and was deposited on the outside bottom of an 8 mol% Y_2O_3 stabilized ZrO_2 solid electrolyte tube (Fig. 1a). The Ag film thickness was on the order of 5 μm and its true surface area was on the order of 2000 cm^2, as estimated from surface titration techniques (*12*). Preparation from Ag paste and surface characterization details have appeared elsewhere (*12*). The ZrO_2 tube was mounted on a gas-tight cylindrical quartz cell (b) with an optically polished flat top by means of a stainless-steel holder (k). This holder had provisions for continuously feeding reactants and removing products through 1.6-mm-o.d. stainless-steel tubes. The cell-to-holder, holder-to-SS tubes, and holder-to-zirconia tube contacts were made gas-tight by means of a ceramic cement paste. The quartz cell was fitted horizontally inside a cylindrical aluminum block furnace possessing a quartz optical window (c). Temperature was measured by a K type thermocouple attached to the inside bottom wall of the ZrO_2 tube, where the Ag reference and counter electrodes were located. The experimental procedure for electro-
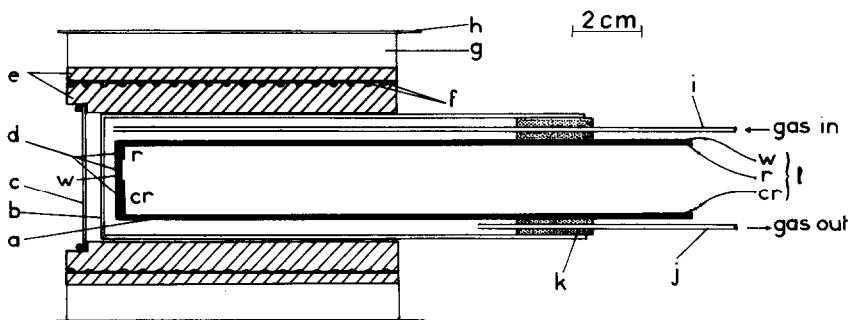
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FIG. 1. Setup of the reactor cell. (a) Zirconia tube; (b) quartz cell; (c) quartz optical window; (d) silver catalyst (w, working electrode; cr, counter electrode; r, reference electrode); (e) aluminum block; (f) heating wire; (g) insulating material; (h) borosilicate tube; (i) gas inlet; (j) gas outlet; (k) stainless-steel holder; (l) leads to r, cr, and w electrodes (see Refs. (11, 14, 17) for details of the solid electrolyte cell construction).

chemically pumping O^{2-} to or from catalyst surfaces has been described elsewhere (11). The experimental setup and procedures for obtaining Raman spectra have also been described recently elsewhere (13). SERS spectra were excited with the 514.5- and/or 488.0-, 457.9-nm lines of a 4W Spectra Physics argon ion laser. The laser light was incident at an angle of 60° on the Ag surface and the scattered light was collected at an angle of 90° with respect to the incident light (horizontal scattering plane).

Cell reactants and products were analyzed by on-line gas chromatography and mass spectrometry as described elsewhere (14). Reactants were L'Air Liquid standard synthetic air (20% O_2–80% N_2) and Scott certified standard of ethylene in nitrogen (3.2% C_2H_4–96.8% N_2).

Two different Ag films were used in the course of the investigation and both showed qualitatively the same behavior.

RESULTS AND DISCUSSION

Figure 2 shows typical SER spectra of the catalyst sample exposed to the O_2/N_2 and to the C_2H_4/N_2 mixtures. After the sample was heated to 675 K and subsequently cooled and left overnight at room temperature under a flow of O_2/N_2 (ca. 100 cm³/min), the Raman spectrum (Fig. 2a) consisted of five bands at wavenumbers

240(sh), 345, 815, 870(sh), and 1630. The positions and relative intensities of these five bands were independent on excitation
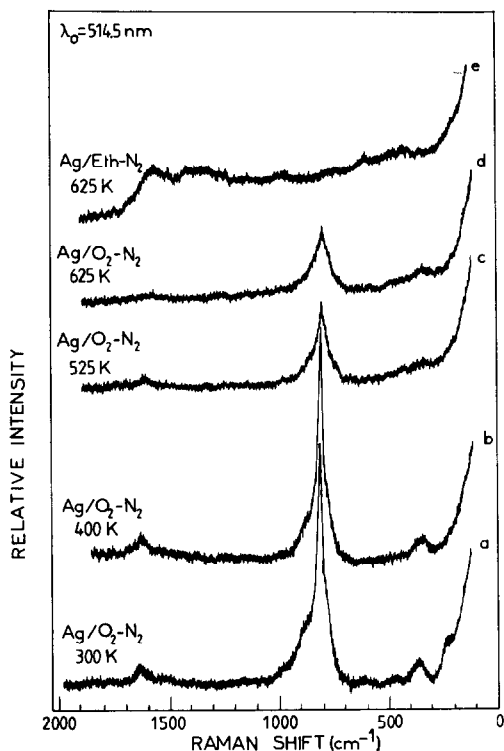

FIG. 2. In situ SER spectra of Ag surface interacting with 20% O_2–80% N_2 at temperatures 300–625 K and with a 3% C_2H_4–97% N_2 mixture at 625 K. $\lambda_0 = 514.5$ nm; laser power, 75 mW; time constant, 0.3 s; resolution, 4 cm^{-1}.

line frequency except for the relative intensity of the 1630-cm^{-1} band, which increased on changing the laser frequency from 514.5 to 457.9 nm. The behavior is analogous to that observed in the preresonance Raman spectra of colored vapors (15) and thus the 1630-cm^{-1} band can be assigned to an overtone of the 815-cm^{-1} band.

On heating the reactor under the flow of air to 400 K, the 240-cm^{-1} band disappeared and the intensities of the other bands seemed to decrease (Fig. 2b). A temperature rise at 525 and 625 K caused a further decrease in the band intensities and the final spectrum at 625 K (Fig. 2d) shows a weak band at 345 cm^{-1} and the strong 815/870 cm^{-1} feature. The intensities of these bands were even further reduced by admitting an air/ethylene mixture flow at 625 K (reaction conditions). When the synthetic air feed was stopped and a 100 cm^3/min flow of a 3% C_2H_4–97% N_2 mixture was admitted at 625 K the SER spectra changed remarkably (Fig. 2e) and displayed broad features centered at wavenumbers 1360 and 1590. This spectral behavior was reversible, i.e., by closing the C_2H_4/N_2 feed and admitting synthetic air the spectrum shown in Fig. 2d quickly reemerged.

The results shown in Fig. 2 indicate that the bands at 240, 345, 815, and 870 cm^{-1} are most probably due to oxygen species adsorbed on silver, while the 1360- and 1590-cm^{-1} bands are due to surface carbon or adsorbed ethylene. Bands in the frequency region 200–500 cm^{-1} have been previously assigned to atomically adsorbed oxygen (Ag–O vibrations) (6, 7), while bands at 815 and 838 cm^{-1} have been attributed to oxygen–oxygen vibrations of an unknown oxygenic species (7). In addition, McBreen and Moskovits (10) have assigned bands at wavenumbers 1370 and 1596 to amorphous surface carbon. It also appears that the relative intensities of the bands at 345 and 815/870 cm^{-1} remain constant with increasing temperature. This is considered as indicating that all these bands are due to the same oxygen–silver species. The fact that

there are no bands observed above 1000 cm^{-1} excludes the possibility of species like O_3^-, O_2^- proposed by Pettenkofer et al. (7). In contrast, the formation of bent type O–Ag–O and/or Ag–O–Ag structures on the surface is very consistent with the appearence of the three bands. For example using the three observed frequencies for a normal coordinate analysis for the O–Ag–O-like molecule, with an angle $\alpha = 120°$ and a Ag–O distance of 2.0 Å, one obtains $F_{Ag-O} = 5.85$, $F_{O-O} = 0.466$, and $F_{Ag-O,O-O} = 0.105$ mdyn/Å, while the Ag–O–Ag-like molecule gives less realistic values for the force constants. Finally, it is noteworthy that the AgO_2-like molecule shows an absorption band in the UV (16) whose tail overlaps with laser lines used to obtain the SER spectra of the present investigation. Such an overlap supports our assignment of the 1630-cm^{-1} band to an overtone with a preresonance enhanced intensity.

Figure 3a shows the dependence of the intensity of the 815-cm^{-1} band, I, on time of exposure in synthetic air, for a prereduced Ag sample at 690 K, i.e., after the sample had been treated with the C_2H_4/N_2 mixture. The reverse process is illustrated in Fig. 3b, which depicts the dependence of I on time of exposure to C_2H_4/N_2 for a preoxidized sample at 690 K. In both cases, the intensity of the 815-cm^{-1} band reaches a steady-state value within 10–15 min. The inserts of Fig. 3 show plots of $\ln (I/I_0)$ vs time for the two processes, where I_0 is the band intensity in synthetic air. By assuming that the intensity of the band at 815 cm^{-1} is proportional to the surface concentration of the oxygen species responsible for this band, one estimates from the slopes of these plots that the first-order rate constants for formation and destruction of this species are 4.2×10^{-3} and 3.6×10^{-3} s^{-1}, respectively.

When synthetic air/C_2H_4 mixtures were fed to the cell it was found that I takes intermediate steady-state values between 0 and I_0. The intensity of the 815-cm^{-1} band is quite sensitive to the O_2/C_2H_4 mole ratio. However, when the Ag catalyst was ex-
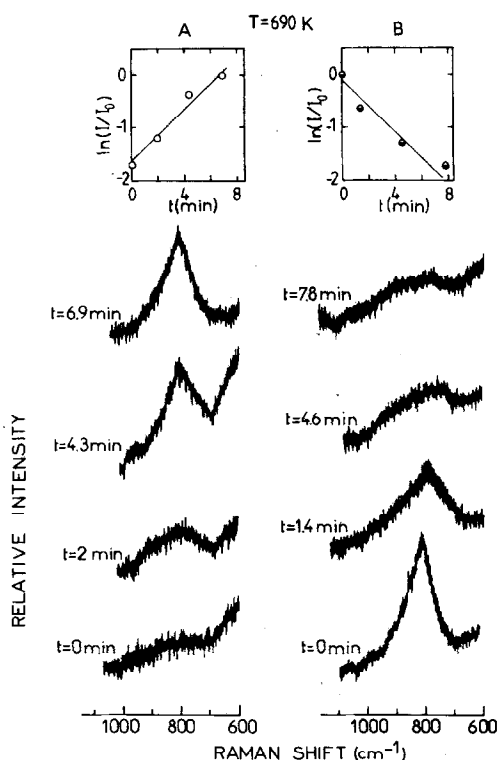
FIG. 3. (A) Time dependence of I upon exposure of a prereduced sample to 20% O_2–80% N_2 at 690 K. (B) Time dependence of I upon exposure of a preoxidized sample to a 3% C_2H_4–97% N_2 mixture at 690 K. For all spectra the optical geometry was the same and $\lambda_0 = 488.0$ nm; laser power, 160 mW; time constant, 0.1 s; resolution, 6 cm^{-1}. For insert plots see text.

posed to electrochemical O^{2-} pumping, no measurable change was observed on I, although the rates of formation of ethylene oxide and CO_2 typically increased by 300% when O^{2-} ions were pumped to the catalyst and an activation overpotential of 350 mV developed at the catalyst–solid electrolyte interface at $P_{ET} = 0.03$ bar, $P_{O_2} = 0.03$ bar, and $T = 690$ K (17).

The above results provide two strong indications that the 815-cm^{-1} oxygen band, which is essentially the only measurable Raman band under reaction conditions, does not originate from a catalytically active surface oxygen species. The first indication comes from examining the magnitude of the time constants for formation and

destruction of the oxygen species corresponding to the 815-cm^{-1} band, i.e., 4.2 × 10^{-3} and 3.6 × 10^{-3} s^{-1} at 690 K. These values are at least two orders of magnitude smaller than typical measured surface oxygen turnover rates during ethylene oxidation to ethylene oxide and CO_2 at this temperature, and on the same catalysts. As an example from Table 2 in Ref. (18) one computes that the total turnover rate of catalytically active oxygen for ethylene oxide and CO_2 formation is on the order of 4.6 s^{-1} at the above referred conditions, i.e., $P_{ET} = 0.03$ bar, $P_{O_2} = 0.03$ bar, and $T = 690$ K. Also from Table 3 in Ref. (18) one computes that the reactive oxygen desorption constant is on the order of 0.1–1 s^{-1} at this temperature.

The second indication that the band at 815 cm^{-1} does not belong to a catalytically active surface oxygen species comes from the fact that the band intensity does not change during O^{2-} pumping, although the catalyst exhibits a rather strong nonfaradaic electrochemical modification of catalytic activity effect (11, 19). It is very difficult to conceive how the rates of ethylene oxide and CO_2 formation could be changing by 300% (between 0 and 0.35 V applied to the catalyst) without any measurable change on I, if the band belonged to a catalytically active oxygen species. In view of the fact that, as previously discussed, the observed Raman frequencies are much more consistent with a dioxygen species O–Ag–O than a Ag–O–Ag species, it is very likely that the observed species is chemisorbed dioxygen which, though present, appears to be catalytically inactive during ethylene epoxidation (20). However, one cannot exclude the possibility that the observed bands might originate from subsurface oxygen which is believed to play an important but indirect role in ethylene epoxidation on Ag (20–22).

CONCLUSIONS

This investigation shows the feasibility of obtaining in situ SERS spectra of Ag cata-

lyst and/or electrode surfaces at temperatures as high as 700 K and atmospheric pressure conditions in conjunction with standard kinetic measurements. The dominant feature of the SERS spectra under reaction conditions is an oxygen band at 815 cm^{-1}. However, our kinetic results show that this band does not belong to the catalytically active surface oxygen species. This raises some questions on how easy it is to monitor catalytically active species on catalyst surfaces.

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