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Interaction of Polycrystalline Silver with Oxygen, Water, Carbon Dioxide, Ethylene, and Methanol: In Situ Raman and Catalytic Studies

Chuan-Bao Wang,[†] Goutam Deo,[‡] and Israel E. Wachs*

Zettlemoyer Center for Surface Studies and Department of Chemical Engineering, Lehigh University, Bethlehem, Pennsylvania 18015

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In situ Raman spectroscopy was used to study the interaction of polycrystalline silver with $^{16}O_2$, $^{18}O_2$, H_2O, D_2O, CO_2, C_2H_4, and CH_3OH at atmospheric pressure and temperatures between 25 and 500 °C. Raman bands at 956 and 800 cm^{-1} were observed upon exposure of silver to $^{16}O_2$, and replacement of $^{16}O_2$ with $^{18}O_2$ shifted these bands to 931 and 778 cm^{-1}, respectively. The 956 cm^{-1} Raman band was assigned to the stretching vibration of surface atomic oxygen with a Ag═O double bond, which sits on top of a Ag atom. This species is stable up to 250 °C and does not appear to interact with water, carbon dioxide, ethylene, or methanol. The 800 cm^{-1} Raman band was assigned to the stretching vibration of surface atomic oxygen with bridging Ag−O−Ag bonds, which sits on the interstices of three Ag atoms. This oxygen species is desorbed above 300 °C and interacts with water, ethylene, and methanol. Upon exposure of preoxidized silver to H_2O and D_2O, a new major Raman band at 866 cm^{-1} was observed, which was also assigned to surface atomic oxygen species, but not surface OH because of the absence of a H/D isotopic effect. The selective oxidation of ethylene and methanol was determined to occur primarily on the surface atomic Ag−O−Ag oxygen species corresponding to the 800 cm^{-1} Raman band.

Introduction

Silver is widely used as an industrial catalyst for the production of ethylene epoxide via ethylene oxidation and for formaldehyde via methanol oxidation.[1] Extensive research has been performed for many decades to elucidate the nature of the active sites and the selective oxidation reaction mechanisms of silver catalysts.[1−5]

Oxygen species on silver were found to play a key role in ethylene epoxidation and selective methanol oxidation. Surface molecular, surface atomic, subsurface atomic, and bulk atomic oxygen species have been reported in the literature. Molecular oxygen was observed on Ag(110) by EELS, which dissociated into surface oxygen atoms above 200 K.[6] Molecular oxygen was also investigated on polycrystalline silver by means of UPS and XPS, which was in good agreement with the single-crystal work.[7] Kilty et al.[8] proposed that molecular oxygen was the active site for the formation of epoxide, whereas atomic oxygen yielded total oxidation of ethylene, on the basis of infrared adsorption studies. In contrast, other authors proposed that adsorbed atomic oxygen is responsible for the epoxidation reaction.[9,10] Surface atomic oxygen was reported to be stable until 600 K[6] and created the active sites for dissociative adsorption of methanol to produce surface methoxy species, which subsequently decomposed to yield formaldehyde.[2] The importance of subsurface atomic oxygen has also been recognized during the past two decades. Grant et al.[11] demonstrated that the presence of subsurface oxygen is necessary for selective oxidation, but not for total oxidation of ethylene. Ertl and Schlogl et al.[12,13] suggested that the subsurface oxygen was involved in the selective ethylene epoxidation and methanol oxidation reactions.

In situ Raman studies on silver catalysts provide unique opportunities to investigate surface oxygen species and other adsorbed species under reaction conditions due to surface-enhanced Raman scattering (SERS) on silver surfaces. Nevertheless, conflicting band assignments from the in situ Raman studies are replete in the catalysis literature. Table 1 summarizes the vibrational band frequencies and assignments on silver obtained from the SERS studies in comparison with other techniques.[6,12,14−22] The great discrepancy in the literature may be related to the silver types (single-crystal, powder, film, and oxide-supported), morphology and surface characteristics (exposed phases, defects and impurities), experimental conditions (vacuum, temperature, and gas-phase compositions), and characterization techniques (EELS, IR, and SERS). In the present work, in situ Raman spectroscopy was employed to systematically investigate the nature of the oxygen species on polycrystalline silver catalysts and their interaction with carbon dioxide, water, ethylene, and methanol in an attempt to elucidate the nature and role of the oxygen species during selective oxidation reactions over commercial polycrystalline silver catalysts.

Experimental Section

In Situ Raman Studies. Electrolytic polycrystalline silver (Handy & Harman, 99.9999%, 30−60 mesh) was investigated. In situ Raman studies were performed using a Spex triplemate spectrometer (Model 1877) equipped with an Ar$^+$ laser (Spectra Physics, Model 171), a Princeton Applied Research OMA III (Model 1461) optical multichannel photodiode array detector, and an in situ cell.[23] A thin self-supporting wafer of ∼200 mg

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* Author to whom correspondence should be addressed at ZCSS, Sinclair Laboratory, 7 Asa Drive, Lehigh University, Bethlehem, PA 18015. Telephone: (610) 758-4274. Fax: (610) 758-6555. E-mail: iew0@lehigh.edu.

[†] Current address: Industrial Scientific Corporation, 1001 Oakdale Road, Oakdale, PA 15071-1500.

[‡] On leave from the Department of Chemical Engineering, Indian Institute of Technology, Kanpar, India.

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TABLE 1: Vibration Frequencies (cm^{-1}) of Oxygen Species on Silver in the Literature

sample	frequency	assignment	technique	adsorption *T*/K	desorption *T*/K	ref
Ag(110)	240	$Ag-O_2$	EELS	100, vacuum	<185	[6]
	325	$Ag-O$			<600	
	640	$AgO-O$			<185	
Ag film	270	$Ag-O$	EELS	80, vacuum		[14]
	645	$Ag[O-O]^{2-}$			<230	
	805	$Ag[O-O]^{2-}$			<230	
	1320	$Ag[O-O]^{-}$			<200	
Ag powder	210	$Ag-O_2$	RAIRS	90, vacuum	<265	[15]
	351	$Ag-O$			<560	
	622	$AgO-O$			<185	
	983	$AgO-O$			<265	
Ag film	335	$Ag-O$	SERS	120, vacuum		[16]
	697	$Ag[O-O]^{2-}$				
	815/838	?				
	1053	$Ag[O-O]^{-}$				
	1286	?				
Ag/SiO_2	676	$Ag[O-O]^{2-}$	SERS	300−465	<400	[17]
	995	$Ag[O-O]^{-}$			>560	
Ag/Al_2O_3	870	$AgO-OC_2H_4$	IR	368		[8]
Ag/YSZ	240	$Ag-O_2$ or O	SERS	298−673	<493	[18]
	345	$Ag-O_2$ or O			<493	
	815	$AgO-O$			>623	
	870	$AgO-O$			<493	
	980	?			<493	
	1630	overtone			?	
Ag/SiO_2	815	$AgO-O$			>623	
	980	?			>623	
Ag/Al_2O_3	805	$AgO-O$			?	
	980	?			?	
Ag powder	436	$Ag-O$, sub	SERS	298−873	873	[19]
	624	$Ag[O-O]^{2-}$			873	
	808	$Ag-O$			873	
	1078	$Ag[O-O]^{-}$			773	
Ag powder	451	$Ag-OH$, sub	SERS	295−873	<670	[20]
	640	$Ag-O$, sub			<870	
	780	$Ag^{III}=O$			>870	
	960	$Ag[O-O]^{-}$			>473	
Ag(111)	554	$Ag-OH$	SERS	298−930	<600	[12,21]
	628	$Ag-O(\beta)$, bulk			830	
	803	$Ag-O(\gamma)$, sub			930	
	860	$Ag-OH$, sub			<900	
	956	$Ag-O(\alpha)$,surf			<580	
	985	$AgOH$ (δ)			<600	
Ag(110)	628	$Ag-O(\beta)$, bulk			<600	
	803	$Ag-O(\gamma)$, sub			930	
Ag_2O	545	$Ag-O$	SERS	300−930	<573	[22]
AgO	430	$Ag-O$			<480	

of pure polycrystalline silver with a thickness of ∼1 mm was placed into the in situ cell and spun at a rate of ∼1500 rpm to dispense local heating caused by laser beams with a spot diameter of ∼1.5 mm. The flow rate through the in situ cell was 100 mL/min for all-gaseous treatments and reactions.

In this work, a standard procedure for preoxidizing silver surface was developed by exposing the silver sample to pure O_2 or 10 mol % O_2 in helium (Ultrahigh Purity, 99.999%, Linde) at 500 °C for 1 h, 300 °C for 1 h, then 200 °C for 2 h. Isotopic experiments were conducted by exposing the silver sample to 5 mol % $^{18}O_2$ in helium (Ultrahigh Purity, 99.999% for both $^{18}O_2$ and helium) using the above standard procedure. The interaction of preoxidized silver with carbon dioxide was examined by flowing pure CO_2 (Instrument Grade, Linde). The interaction of preoxidized silver with distilled water and deuterium oxide (99.96 atom/D, Isotech Inc.) was achieved by flowing He (Ultrahigh Purity, 99.999%, Linde) through a saturator containing water or deuterium oxide at 22 °C. Ethylene oxidation was carried out with a gaseous reactant mixture of $C_2H_4/O_2/He = 25/7/68$ (molar ratio) in the temperature range of 200−250 °C. Ethylene used was purchased from Linde with a purity of >99.5% (CP grade). Methanol oxidation was conducted with $MeOH/O_2/He = 4.2/1.4/84.4$ (molar ratio) and a total flow rate of 100 mL/min in the temperature range of 250−500 °C. Methanol (Semiconductor grade, 99.9%) was from Alfa Aesar. An on-line mass spectrometer was employed to detect the reaction products from the in situ Raman cell. The MS studies demonstrated that very high CH_3OH conversions, greater than 50%, and low C_2H_4 conversions, less than 5%, were achieved in the Raman cell with the polycrystalline silver wafer. More quantitative kinetics data were obtained with conventional fixed-bed reactor studies.

Catalytic Studies on Methanol Oxidation. Methanol oxidation over 50 mg of the Handy & Harman silver (99.9999%, 30−60 mesh) was performed in a fixed-bed reactor (∼5 mm i.d.) at atmospheric pressure and in the temperature range 250−500 °C. Quartz wool was packed below the catalyst bed to support the catalyst. A thermocouple was placed to contact with the outside wall of the catalyst bed for temperature monitoring. A reactant stream of $CH_3OH/O_2/He = 6.16/2.0/91.8$ (molar ratio) with a total flow rate of 100 mL/min was used. An on-line HP 5890II GC, equipped with a Carboxene-1000 packed and a CP-sil 5 CB capillary columns for TCD and FID detectors, respectively, was used to analyze the reactants and products.

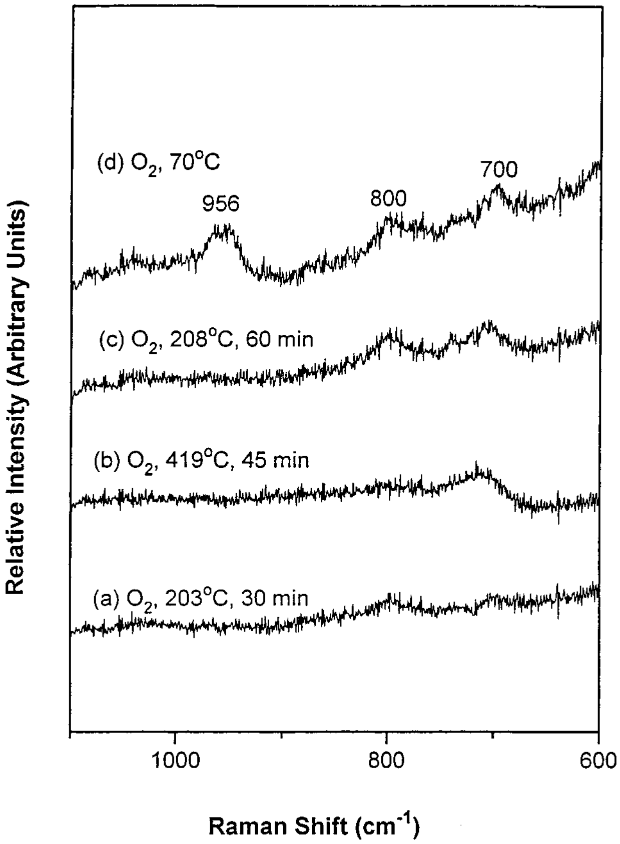

Figure 1. Typical in situ Raman spectra of fresh polycrystalline silver after first- and second-cycle thermal treatment under $^{16}O_2$ flow.

The fixed-bed reactor studies were critical to guiding the experimental conditions for the in situ Raman reaction studies.

Results

Interaction with $^{16}O_2$ and $^{18}O_2$. It was found that fresh silver usually exhibited very weak Raman features after the first-cycle thermal treatment (25−500 °C) under oxygen flow. Typical Raman spectra in the 600−1200 cm^{-1} region during the first- and second-cycle thermal treatments are presented in Figure 1. The 600−1200 cm^{-1} spectral region was focused on in this work since Raman bands due to the stronger stretching vibrations are generally located in this region. Spectrum (a) was obtained at 203 °C after heating the silver sample at 500 °C for 1 h followed by 300 °C for 1 h. It can be seen that only very weak Raman features at 800 and 700 cm^{-1} are present in the spectrum. In the second-cycle, increasing the temperature to 419 °C led to disappearance of the weak feature at ∼800 cm^{-1} (Figure 1b). Upon decreasing the temperature to 208 °C during the second cycle, the weak Raman band at ∼800 cm^{-1} emerged again (Figure 1c). Further decrease in temperature to 70 °C resulted in the presence of a third weak Raman band at ∼956 cm^{-1} (Figure 1d). Extremely weak Raman bands at ∼1050 cm^{-1} may be due to trace amounts of surface carbonate or nitrate species.

To achieve intense and reproducible Raman bands due to oxygen species on silver, the sample was further exposed to a number of cycles of heating and slow cooling between 25 and 500 °C. It is well-known that surface morphology plays an important role in surface-enhanced Raman scattering (SERS).[24,25] Heating the silver sample at high temperatures in an oxygen atmosphere creates rough silver surfaces by large-scale surface reconstruction,[13,26] which is necessary by SERS.

The development of the Raman spectra while decreasing the sample temperature from 416 °C to room temperature (RT, 25 °C) under flowing O_2 is shown in Figure 2. At high temperatures (309 and 416 °C), Raman bands were absent. At 195 °C, two Raman bands at ∼956 and ∼800 cm^{-1} due to oxygen species appeared. Both of them increased in intensity upon decreasing the temperature to 25 °C.

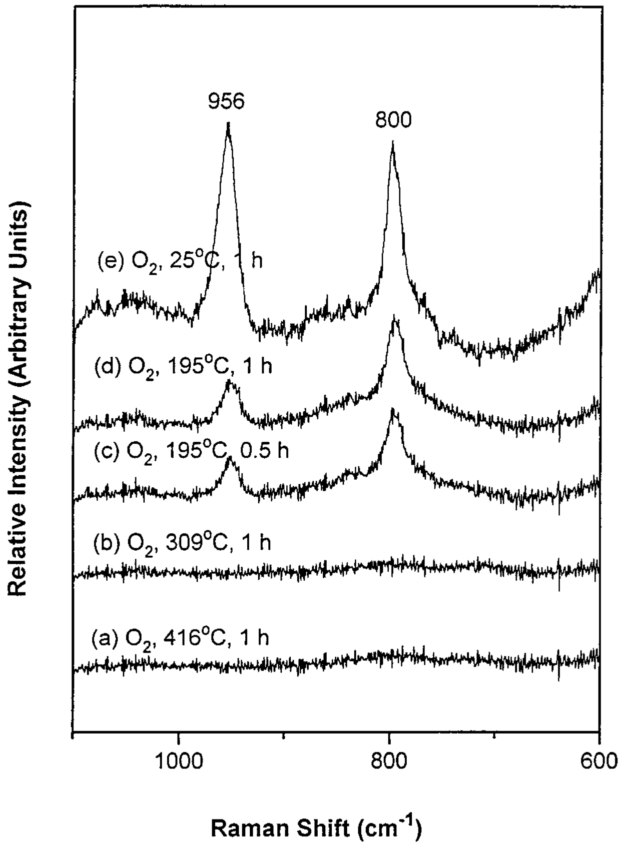

Figure 2. In situ Raman spectra of polycrystalline silver in the course of decreasing the sample temperature from 416 °C to room temperature (RT) under $^{16}O_2$ flow.

The typical development of the Raman spectra of a preoxidized silver in the course of increasing temperature from 27 to 440 °C under an O_2/He (10 mol % oxygen) flow is shown in Figure 3. The Raman spectrum of Figure 3a was taken after the silver sample was thermally treated in an O_2 stream according to the standard procedure described in the Experimental Section and then kept in an O_2 stream overnight at room temperature (27 °C). Subsequent heating to 201 °C in the O_2/He flow resulted in a slight decrease in intensity of both the ∼956 and ∼800 cm^{-1} bands (Figure 3b). Further heating to 262 °C (Figure 3c) under the O_2/He flow caused substantial desorption of the oxygen species responsible for the 956 cm^{-1} band. The different thermal stability of these two Raman bands indicates that they originate from two different oxygen species on silver. At 320 and 440 °C, the Raman bands at 956 and 800 cm^{-1} disappeared due to complete desorption of the oxygen species from the silver surface.

The development of the Raman spectra of preoxidized silver in the course of increasing temperature under He flow is illustrated in Figure 4. Flowing He at room-temperature overnight (Figure 4b) resulted in a slight diminution of both 956 and 800 cm^{-1} bands. Heating the catalyst to 199 °C in He flow substantially reduced the Raman band at 956 cm^{-1}. The Raman bands at 956 and 800 cm^{-1} completely disappeared upon further heating the silver catalyst to 261 and 320 °C. Following cooling to 201 °C in flowing He caused reappearance of a weak Raman band at 956 cm^{-1}, which may have originated from trace

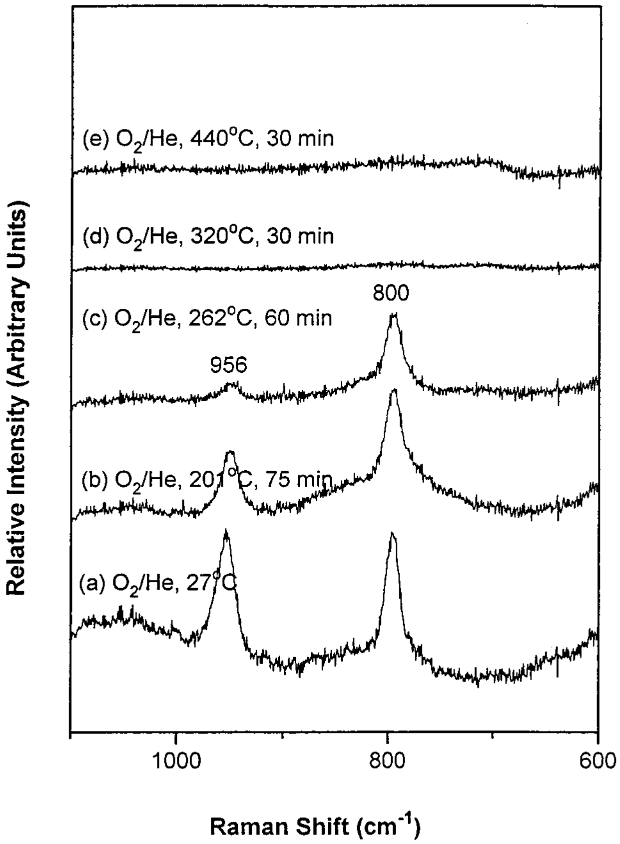

Figure 3. In situ Raman spectra of preoxidized polycrystalline silver in the course of increasing the temperature from 27 to 440 °C under $^{16}O_2$/He flow.

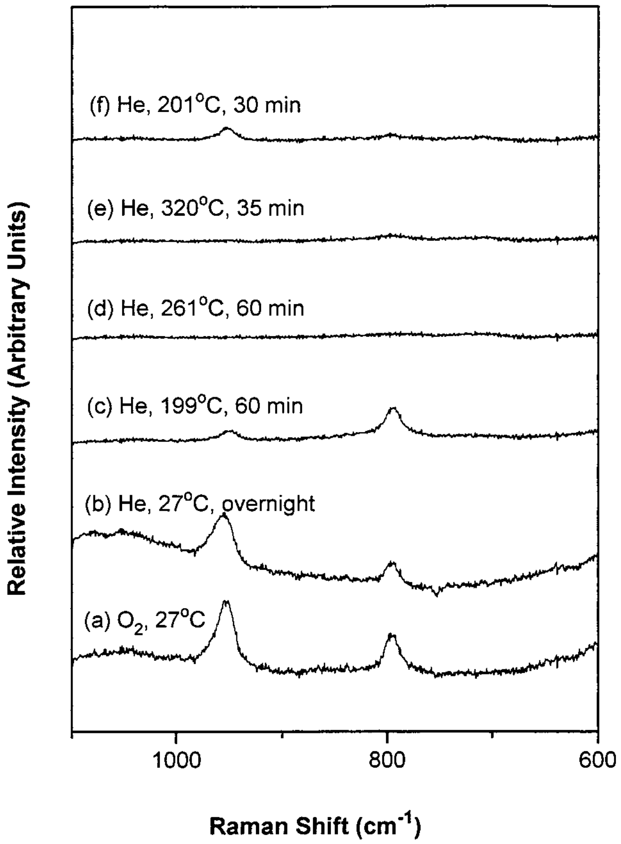

Figure 4. In situ Raman spectra of preoxidized polycrystalline silver in the course of increasing the temperature from 27 to 320 °C under He flow.

amounts of O_2 in the He stream. Compared to the results in the presence of O_2, it can be seen that the oxygen species responsible for the 956 and 800 cm^{-1} bands desorb at relatively low temperatures, and that the 956 cm^{-1} species desorbs at even lower temperatures.

Isotopic experiments using $^{18}O_2$/He verified that the 956 and 800 cm^{-1} Raman bands correspond to oxygen species on silver. The in situ Raman spectra of silver preoxidized with isotopic $^{18}O_2$ are shown in Figure 5. Two new bands at ~931 and ~778 cm^{-1} (positioned by curve fitting) appeared along with the 956 and 800 cm^{-1} bands upon the standard thermal treatment under $^{18}O_2$/He flow, as shown in Figure 5a. Concurrent existence of the 956 and 800 cm^{-1} bands with the isotopic bands during $^{18}O_2$/He treatment reveals that a large amount of oxygen is dissolved in the silver bulk. The dissolved oxygen could migrate and repopulate the oxygen species responsible for the 956 and 800 cm^{-1} bands. The distribution of the oxygen isotopes over the different oxygen sites resulted in somewhat weaker Raman signals for each individual oxygen species. Further heating the sample at 200 °C for 4 h under $^{18}O_2$/He resulted in a substantial decrease of the 800 cm^{-1} Raman band relative to the ~778 cm^{-1} shoulder. The 800 cm^{-1} Raman band became very intense when $^{18}O_2$/He was stopped and $^{16}O_2$/He was introduced at 200 °C for 2 h. The isotopic shifts confirm that the bands at 956 and 800 cm^{-1} correspond to the vibrations of oxygen species

The magnitudes of the isotope shifts for the 956 and 800 cm^{-1} Raman bands are 24 and 20 cm^{-1}, respectively, which are significantly smaller than isotopic shifts previously observed for O−O stretching vibrations of molecular oxygen species on silver and in matrix $Ag^+O_2^-$ studied by SERS and RAIRS at low temperatures (32−61.1 cm^{-1}).[27−30] Thus, the 956 and 800 cm^{-1} Raman bands are associated with atomic oxygen species on silver.

Interaction with H_2O and D_2O. Interactions of preoxidized silver with H_2O and D_2O were investigated in order to determine whether the surface oxygen species react with water and deuterium oxide.

In situ Raman spectra of preoxidized silver upon exposure to a H_2O/He (4/96) mixture is presented in Figure 6. Prior to introducing H_2O/He into the in situ cell, the silver sample was oxidized by pure O_2 using the standard procedure described in the Experimental Section, and then cooled from 200 to 62 °C under flowing He. The Raman spectrum taken at 62 °C (see Figure 5a) showed the presence of Raman bands at 956 and 800 cm^{-1} due to the atomic oxygen species. Two new Raman bands at 963 and 866 cm^{-1} appeared upon exposure to H_2O/He, indicating the development of new Raman-active species on the silver surface. When the sample was heated to 196 °C in the presence of flowing H_2O/He, the water-induced bands at 963 and 866 cm^{-1} substantially diminished in intensity. The 800 cm^{-1} Raman band, which was stable above 260 °C under flowing O_2 as shown in Figure 3, also diminished somewhat in intensity along with the water-induced bands even at a temperature as low as 196 °C under the flowing H_2O/He environment. When the silver sample was further cooled to 46 and 28 °C in flowing H_2O/He, the Raman bands at 963, 866, and 800 cm^{-1} again became intense.

Very similar Raman spectra were obtained when H_2O was replaced by D_2O, as shown in Figure 7. The 953 and 800 cm^{-1} bands were present after the silver sample was treated using the standard procedure and cooled to 40 °C in 10 mol % O_2 in helium (see Figure 7a). Intense Raman bands at 963, 866, and

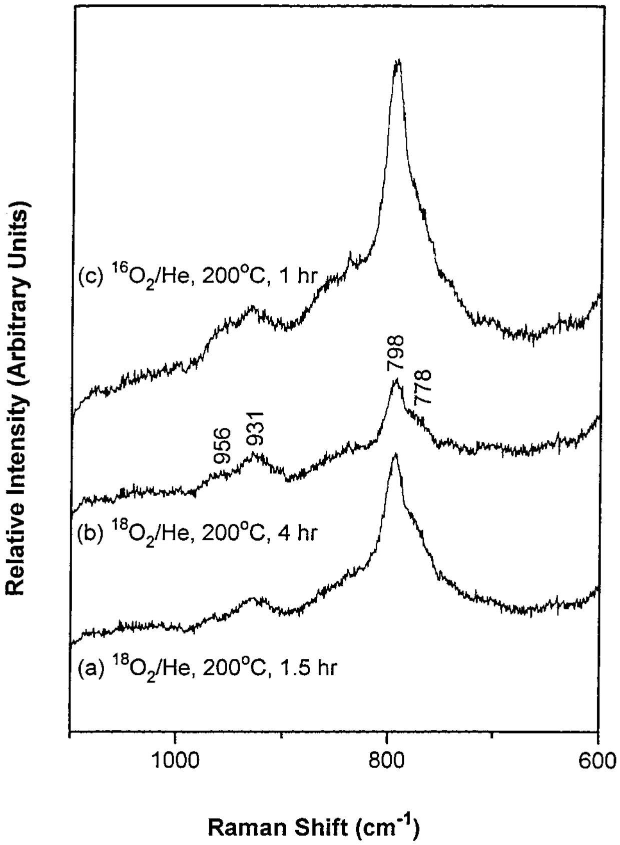

Figure 5. In situ Raman spectra of polycrystalline silver in the course of being pretreated (a) with $^{18}O_2$ and (b) followed by $^{16}O_2$.

790−800 cm^{-1} are present upon exposing the sample to flowing D_2O/He at room temperature (40 °C, see Figure 7b). The bands induced by D_2O are essentially at the same frequencies as those induced by H_2O, which strongly suggests that the water-induced species is not related to OH (or OD) groups because of the absence of an isotopic effect. Heating the sample at 200 °C for 45 min caused almost complete disappearance of the 866 and 790−800 cm^{-1} bands (see Figure 7c). This observation suggests that the oxygen species responsible for the 800 cm^{-1} band may combine with the water-induced oxygen species to desorb at lower temperatures since the desorption temperatures of the oxygen species corresponding to the 800 cm^{-1} band are higher than 200 °C in the presence of oxygen or helium (see Figures 3 and 4). Further heating the sample to 250−400 °C leads to almost complete absence of any observable Raman bands (see Figure 7e,f). No observable Raman bands are formed during the course of cooling the sample back to 58 °C, indicating that preoxidized silver surface is critical for the formation of the water-induced oxygen species. Compared to the case in Figure 6, heating to higher temperatures (300−400 °C) led to the complete desorption of oxygen species and, thus, the features at 963, 866, and 800 cm^{-1} did not reappear in Figure 7g.

To investigate the effects of oxygen present during interaction with deuterium oxide, experiments were also conducted by adding O_2 into the D_2O/He gaseous stream. The corresponding in situ Raman spectra are presented in Figure 8. Two drastic differences were observed in the presence of O_2: (a) the 800 cm^{-1} band remained upon heating the sample to 200−250 °C, indicating that the additional O_2 supplied the oxygen species corresponding to the 800 cm^{-1} band, and (b) the Raman features were readily observed in the course of cooling the sample. These results further confirm that the simultaneous disappearance of the 800 cm^{-1} band with the 866 cm^{-1} band in Figure 7 is caused by consumption, but not simple desorption of the oxygen species corresponding to the 800 cm^{-1} band.

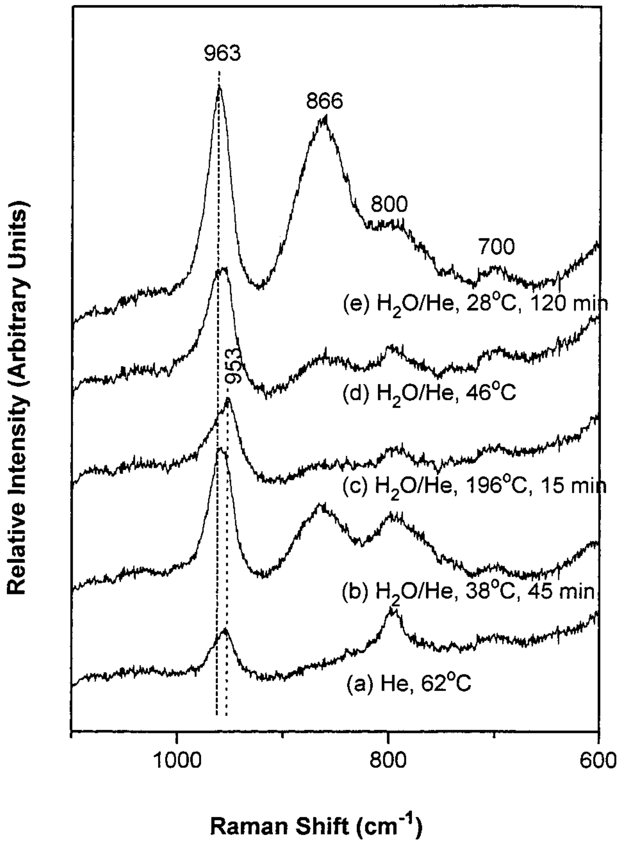

Figure 6. In situ Raman spectra of preoxidized polycrystalline silver obtained upon exposure to H_2O vapor with a gas stream of H_2O/He = 4/96.

The in situ Raman spectra of the nonpreoxidized silver during flowing D_2O/He are shown in Figure 9. The Raman spectrum obtained upon thermal treatment (500 °C 1 h, 300 °C 1 h, then 200 °C 2 h, and finally cooled to 33 °C) under helium flow does not possess any obvious bands due to oxygen species (see Figure 9a). Upon exposing the sample to D_2O/He flow at 30 °C, an intense Raman band at 963 cm^{-1} and weaker bands at 866 and 800 cm^{-1} slowly developed, which further confirms that a preoxidized silver surface is required for efficient formation of the water-induced oxygen Raman bands. Subsequent addition of O_2 into the gas stream caused a slight increase in the intensity of both bands.

Interaction with CO_2. The in situ Raman spectra of preoxidized silver interacting with CO_2 are shown in Figure 10. After exposing the silver catalyst sample to pure CO_2 at 30 °C for 45 min, the 956 and 800 cm^{-1} bands essentially do not change and no new Raman bands due to surface carbonate species are present (see Figure 10b). Previous in situ Raman studies revealed that CO_2 could react with surface atomic oxygen species to form a surface carbonate at 50 K, which exhibits intense Raman bands at 682, 703, 1046, 1289, and 1420 cm^{-1}.[31] Upon increasing the sample temperature to 200 °C, the band at 800 cm^{-1} appears to considerably diminish possibly due to partial desorption of this oxygen species (see Figure 10c). Work by Bowker et al.[32] showed that an adsorbed carbonate species on Ag(110) decomposed to yield CO_2 and O_a upon heating to 485 K. The absence of detectable adsorbed carbonate species in the present study may also be related to the saturation of the silver surface with atomic oxygen species. Backx et al.[33] have found that the amount of adsorbed CO_2 becomes smaller at

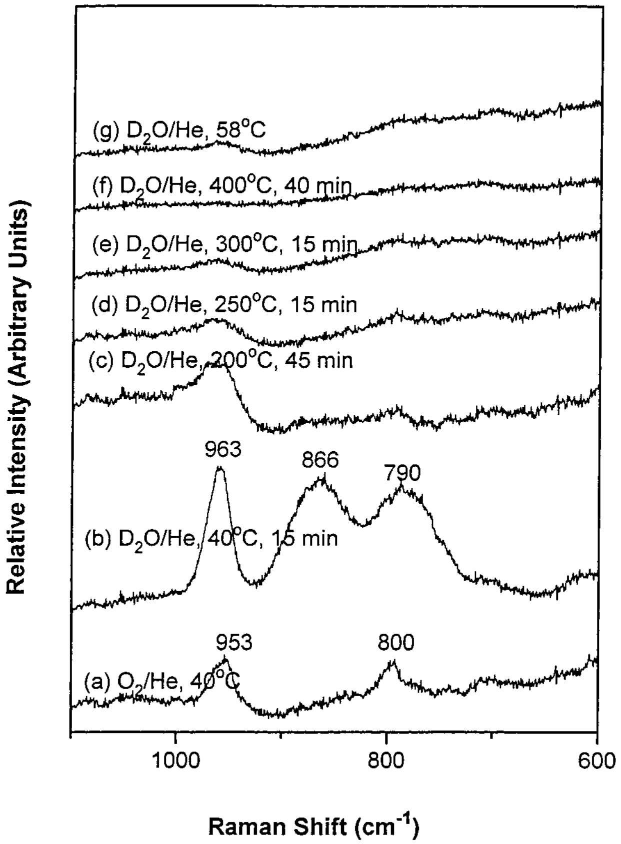

Figure 7. In situ Raman spectra of preoxidized polycrystalline silver obtained upon exposure to D_2O vapor with a gas stream of $D_2O/He = 4/96$.

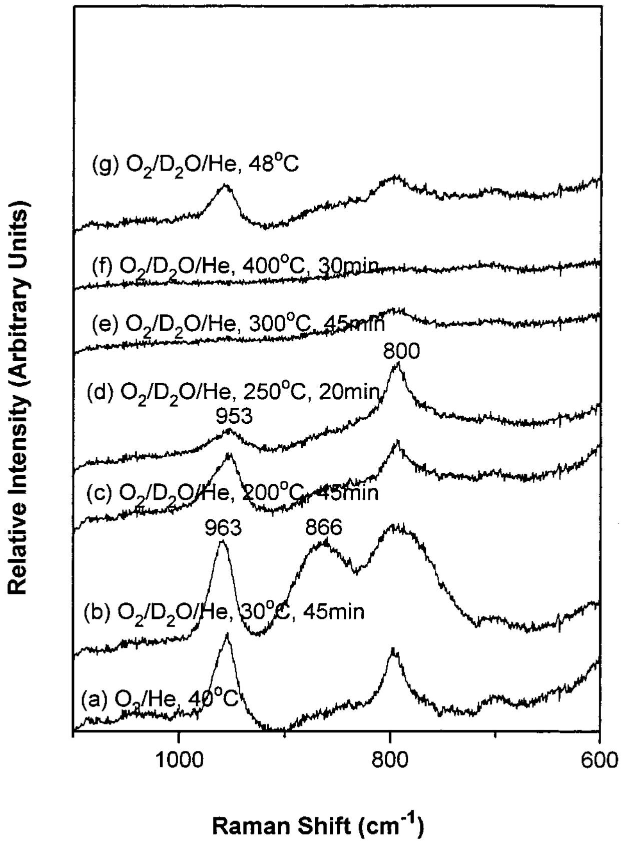

Figure 8. In situ Raman spectra of preoxidized polycrystalline silver obtained upon exposure to D_2O vapor with a gas stream of $D_2O/O_2/He = 4/48/48$.

oxygen coverage higher than 0.25. Barteau et al.[34] also previously observed by TPD that the amount of CO_2 adsorbed per oxygen atom decreased when increasing surface oxygen coverages. In the present study, the preoxidized silver surface is close to full coverage by oxygen and, consequently, it is not surprising that only a small amount of surface oxygen is interacting with CO_2. The extremely weak Raman band at ~1050 cm^{-1} may originate from trace amounts of surface carbonate species, but this band is essentially indistinguishable from background noise. Thus, the absence of surface carbonate in the present study is consistent with prior literature findings.

Interaction with C_2H_4. The interaction of preoxidized silver with C_2H_4 was also investigated. The 956 and 800 cm^{-1} bands were clearly present at 201 °C after the standard treatment under flowing O_2, shown in Figure 11a. When the O_2 flow was stopped and the sample was exposed to an C_2H_4/He mixture at 201 °C for 15−105 min, the intensity of the 800 cm^{-1} band significantly decreased, but the intensity of the 956 cm^{-1} band remained essentially unchanged (see Figure 11b−d). Upon increasing the sample temperature to 252 °C, the 800 cm^{-1} Raman band further decreased in intensity. At a temperature of 252 °C, the 956 cm^{-1} band also decreased in intensity because of partial desorption of this adsorbed oxygen species.

The in situ Raman spectra of ethylene oxidation over polycrystalline silver at reaction temperatures and an C_2H_4/O_2 ratio close to industrial conditions for the oxygen-based direct oxidation process[35] are presented in Figure 12. Exposing the sample to an ethylene oxidation stream (molar ratio of $C_2H_4/O_2/He = 25/7/68$) at 201 °C led to a decrease in intensity of the 800 cm^{-1} band (see Figure 12b,c) and this Raman band further decreased in intensity upon increasing the temperature to 252 °C for 45 min. The Raman band at 956 cm^{-1} was observed to decrease slightly upon exposure to the ethylene oxidation stream at 201 °C, and a significant decrease in its intensity occurred when the temperature was increased to 252 °C primarily due to thermal desorption of this oxygen species.

The silver sample was preoxidized with $^{18}O_2$/He (500 °C 1 h, 300 °C 1 h, and 250 °C 0.5 h) in order to follow the fate of the two different oxygen species during ethylene oxidation in an $C_2H_4/^{16}O_2$/He environment. Raman features at about 956 and 800 cm^{-1} due to the ^{16}O species and at 931 and 778 cm^{-1} due to ^{18}O species were initially present in the Raman spectrum, as shown in Figure 13a. Switching to a $C_2H_4/^{16}O_2$/He stream at 250 °C resulted in a decrease in intensity of the 800 and 780 cm^{-1} Raman bands and a slight growth of the ~956 cm^{-1} band due to ^{16}O species. It is interesting to note that the 931 cm^{-1} band due to ^{18}O species essentially remained unchanged. These results suggest that the oxygen species corresponding to the 800 and 780 cm^{-1} bands preferentially participated in ethylene oxidation.

Interaction with CH_3OH. In situ Raman studies were also conducted during methanol oxidation over polycrystalline silver under steady-state reaction conditions (molar ratio of MeOH/O_2 = 3 and up to 500 °C). The methanol/oxygen ratio is close to that employed in industrial processes.[35] The initial state of the preoxidized silver surface after the sample was pretreated with $^{18}O_2$/He at high temperatures (500 °C 1 h, 300 °C 1 h, and 250 °C 2 h) is shown in Figure 14a. Exposure to a MeOH/$^{16}O_2$/He gas mixture under flowing conditions caused reduction of the 800 and 778 cm^{-1} bands at 250 °C due to the continuous consumption of the oxygen species during the net reducing environment of methanol oxidation reaction (molar ratio of $CH_3OH/O_2 = 3$). Increasing the reaction temperature to 350−500 °C leads to development of a very broad feature at 870−700

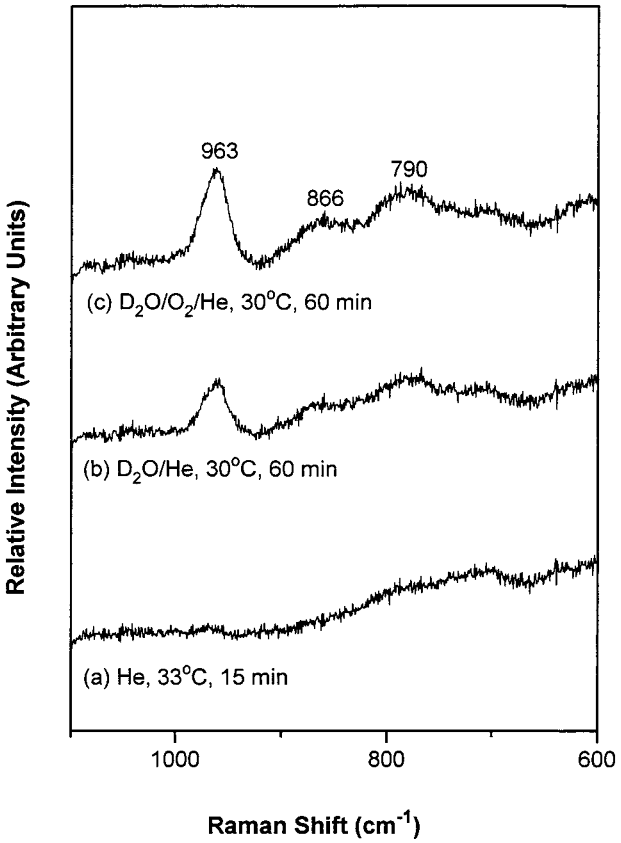

Figure 9. In situ Raman spectra of polycrystalline silver without preoxidation treatment obtained upon exposure to D_2O vapor with a gas stream of $D_2O/He = 4/48$, followed by $D_2O/O_2/He = 4/48/48$.

cm^{-1}, indicating the presence of the surface oxygen species corresponding to the 800 and 780 cm^{-1} bands as well as other species. The 870 cm^{-1} band may be actually the same oxygen species as the water-induced oxygen species (see Figures 6−8). The results in this work indicate that the oxygen species related to the 870 and 800 cm^{-1} bands are slightly stabilized under methanol oxidation conditions, as evidenced by the presence of these bands at reaction temperatures of 350−500 °C.

Catalytic Behavior of Methanol Oxidation. The catalytic properties of polycrystalline silver were investigated in a fixed-bed reactor over the temperature range 250−500 °C and are presented in Table 2. The conversion of methanol increases from 15.9 to 81.4% upon increasing the reaction temperature from 250 to 500 °C. All the oxygen in the reaction mixtures was consumed at temperatures above 250 °C and the production of H_2 during this reaction is well-known. Significant amounts of methylformate and CO_2 were also formed at temperatures lower than 350 °C. The formation of formaldehyde increased with increasing temperature and reached a selectivity of 92.5% at 500 °C. The increasing formaldehyde selectivity with temperature is due to the lower surface methoxy concentration, lower probability of surface intermediates forming methylformate, and lower probability of over-oxidation to CO_2. The data presented here are in good agreement with those reported by Lefferts et al.[36]

The effect of the $MeOH/O_2$ ratio on the catalytic properties of methanol oxidation was also examined (shown in Table 3). Upon decreasing the $MeOH/O_2$ molar ratio from 3.08 to 0.95, the methanol conversion increased from 78.0 to 98.4% with a drastic decrease in formaldehyde selectivity since excess oxygen leads to combustion of formaldehyde to carbon dioxide.

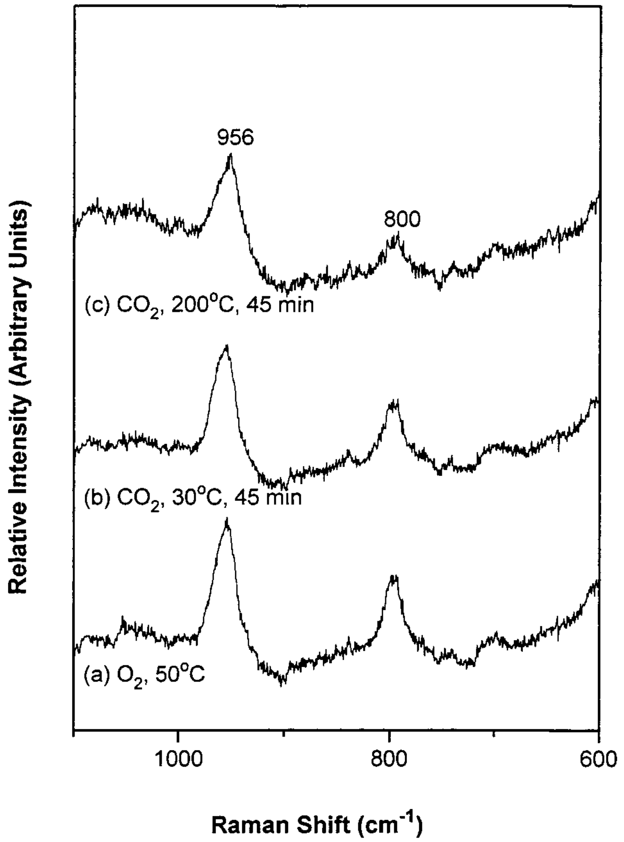

Figure 10. In situ Raman spectra of preoxidized polycrystalline silver interacting with CO_2 at 30 and 200 °C.

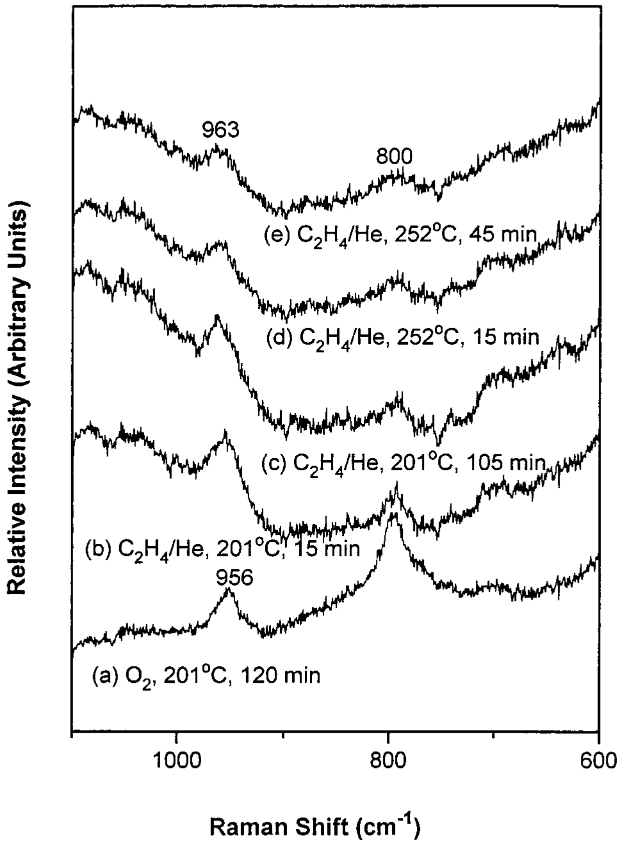

Figure 11. In situ Raman spectra of preoxidized polycrystalline silver obtained upon exposure to C_2H_4/He.

The results presented here demonstrate that (1) methanol conversion and formaldehyde selectivity of methanol oxidation

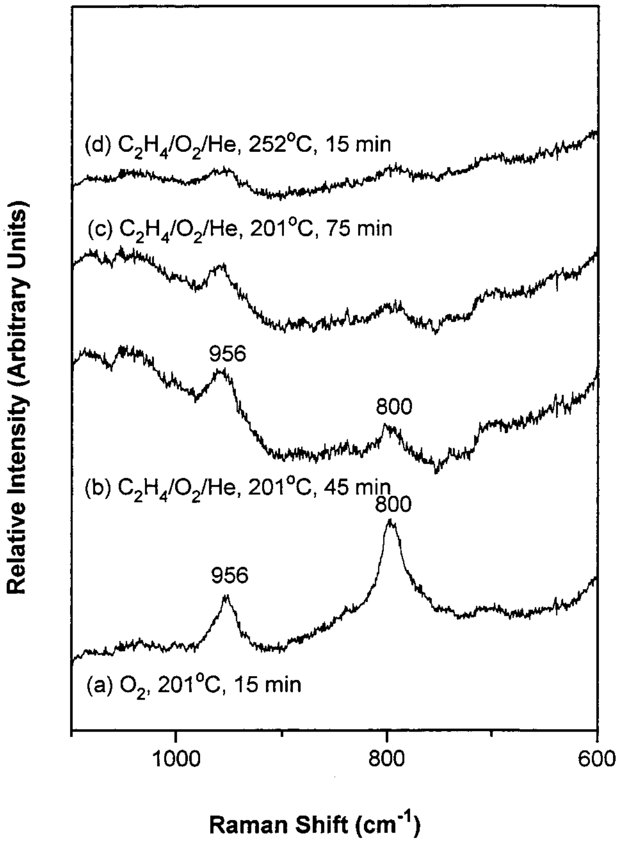

Figure 12. In situ Raman spectra of preoxidized polycrystalline silver obtained upon exposure to $C_2H_4/O_2/He$.

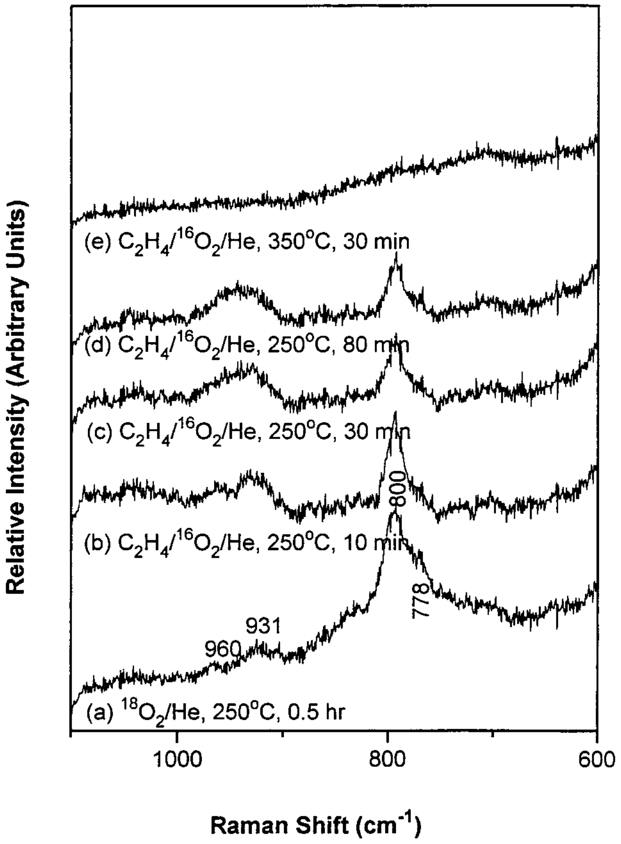

Figure 13. In situ Raman spectra of $^{18}O_2$-preoxidized polycrystalline silver obtained upon exposure to $C_2H_4/O_2/He$.

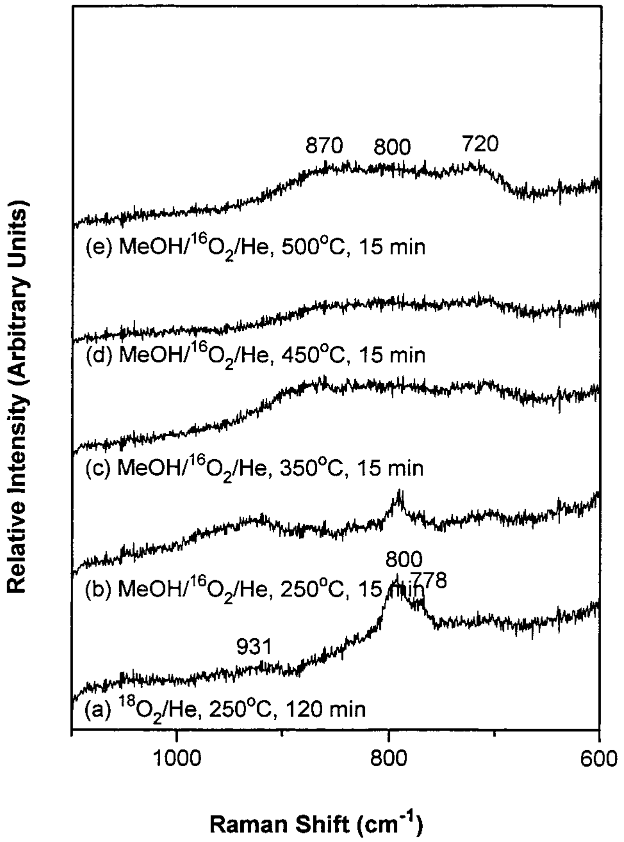

Figure 14. In situ Raman spectra of $^{18}O_2$-preoxidized polycrystalline silver obtained upon exposure to $MeOH/O_2/He$.

TABLE 2: Methanol Conversion and Product Selectivities Formed over 50 mg of a Polycrystalline Ag Catalyst with a Methanol Concentration of 6.16 mol% and a Total Flow Rate of 100 mL/min (helium used as balance gas) at a Molar Ratio of $MeOH/O_2 = 3.08$

	conv. (%)	selectivity			
T (°C)	MeOH	HCHO	MF	DMM	CO_2
250	15.9	29.9	47.0	0.0	23.1
300	39.8	42.1	28.2	0.3	29.4
350	55.8	69.9	13.4	0.2	33.5
400	69.0	83.8	5.7	0.2	9.5
450	79.8	90.0	2.1	0.1	7.8
500	81.4	92.5	0.8	0.0	6.7

TABLE 3: Methanol Conversion and Product Selectivities Formed over 50 mg of a Polycrystalline Ag Catalyst with a Methanol Concentration of 6.16 mol% and a Total Flow Rate of 100 mL/min (helium used as balance gas) at 500 °C

	conv. (%)	selectivity		
molar ratio of $MeOH/O_2$	MeOH	HCHO	MF	CO_2
3.08	78.0	92.3	0.9	6.8
2.80	89.3	89.3	0.8	9.9
2.46	90.6	87.4	0.6	12.0
2.05	94.9	85.0	0.5	14.5
1.49	99.4	75.1	0.3	24.6
0.95	98.4	69.1	0.3	30.6

at 500 °C essentially approaches those in an industrial process, where the reactor temperature is 650 °C; (2) methanol/oxygen molar ratio is very important and, thus, a correct ratio should be applied for in situ Raman studies of methanol oxidation over silver catalysts.

Discussion

Nature of Oxygen Species on Silver. In the present study, intense Raman bands at 956 and 800 cm^{-1} were observed in

TABLE 4: Band Positions of O−O Vibrations Observed upon Exposure of Silver to $^{16}O_2$ and $^{18}O_2$ at Temperatures Lower than 120 K in Comparison to Stretch Frequencies in Matrix $Ag^+O_2^-$

species	ν_{16}/ cm^{-1}	ν_{18}/ cm^{-1}	$(\nu_{16}-\nu_{18})$/ cm^{-1}	(ν_{18}/ν_{16})/ cm^{-1}	technique	ref
$O_2 \rightarrow Ag$	697	665	32	0.954	SERS	[16]
	1053	1004	49	0.953		
$O_2 \rightarrow Ag$	622	585	37	0.941	RAIRS	[15]
	983	928	55	0.944		
$Ag^+O_2^-$	1084.4	1023.3	61.1	0.944	SERS	[29]
	1078.9	1018.3	60.6	0.944		
$O \rightarrow Ag$	800	780	20	0.973	SERS	this work
	956	931	25	0.974		

the temperature range 20 to 260 °C when polycrystalline silver was pretreated in flowing $^{16}O_2$ at elevated temperatures. The 800 cm^{-1} band is thermally more stable than the 956 cm^{-1} band (see Figures 3 and 4), indicating that the two bands come from different species. When $^{16}O_2$ is replaced with $^{18}O_2$, these bands shift to 931 and 778 cm^{-1}, respectively. The isotopic shift unambiguously confirms that the 956 and 800 cm^{-1} bands originate from the vibration of oxygen species.

Furthermore, the magnitudes (20−25 cm^{-1}) and $\nu(^{18}O)/\nu(^{16}O)$ ratios (0.973−0.974) of the isotopic shifts also suggest that the bands corresponding to 956/931 and 800/778 cm^{-1} involve atomic oxygen species. It is well documented in the literature[15,16,29] that isotopic shifts (summarized in Table 4) of O−O stretching vibrations for adsorbed molecular oxygen species on silver at low temperatures (<120 K) and matrix isolated $Ag^+O_2^-$ are in the range 32−37 cm^{-1} for vibrations at ∼600 cm^{-1} and 49−61.1 cm^{-1} for vibrations at ∼1000 cm^{-1}, which are significantly larger than those observed in the present investigation. Wang et al.[15] unambiguously identified the band at 983 cm^{-1} at 90 K as resulting from molecularly adsorbed oxygen species by isotopic experiments and reflection−absorption infrared spectroscopy (RAIRS). In his work, the 983 cm^{-1} band shifted to 928 cm^{-1} when $^{16}O_2$ was replaced with $^{18}O_2$. Furthermore, three bands at 983, 957, and 928 cm^{-1}, with the middle one twice the integrated intensity of the $^{16}O_2$ and $^{18}O_2$ bands, were obtained when $^{16}O_2$ was replaced with an equilibrium mixture of the two oxygen isotopes, namely, $^{16}O_2 + 2^{16}O^{18}O + {}^{18}O_2$. Oyama et al.[36b] observed an adsorbed peroxide species on MnO with Raman signal at 884 cm^{-1} during reaction conditions at higher temperatures. The $\nu(^{18}O)/\nu(^{16}O)$ value of this adsorbed species was 0.946 with an isotopic shift of 47 cm^{-1}, in excellent agreement with the ratio calculated for a peroxide species (0.943) by using a harmonic oscillator model. Ab initio MO calculation confirmed this assignment, using $Mn(OH)_4(O_2)^+$ as a model compound for the adsorbed species. This work is in good agreement with the work in Table 4 done at low temperatures where the oxygen species were molecular species. Similarly, Lunsford et al.[36c] observed a peroxide ion on Ba/MgO catalysts with an isotopic shift of 47 cm^{-1} and a $\nu(^{18}O)/\nu(^{16}O)$ value of 0.946 at 700 °C.

It was generally claimed that the adsorbed molecular oxygen species was only stable at low temperatures over silver. Backx et al.[37] reported that molecular oxygen on Ag(110) was a weakly bound species, which readily desorbed or dissociated into two atoms above 170 K. Grant et al.[38] claimed that molecular oxygen existed on Ag(111) up to a temperature of 380 K on the basis of isotope-exchange TPD experiments. Campbell et al.[39] also studied molecular oxygen on Ag(111), but could not reproduce the stable molecular oxygen species even at 380 K reported by Grant.

In contrast, other researchers proposed that adsorbed molecular oxygen species were also present on silver at elevated temperatures. Kilty et al.[8] observed an IR band at 870 cm^{-1} after exposing preoxidized Ag/SiO_2 and $Ag/\gamma\text{-}Al_2O_3$ samples to ethylene at 368 K, which was assigned to the O−O vibration of an organic peroxide group, C_2H_4−O−O−Ag. When using $^{16}O_2$ and $^{18}O_2$ to replace $^{16}O_2$, two bands at 870 and 848 cm^{-1} were observed with an isotopic shift of 22 cm^{-1}. Kondarides et al.[18] observed a Raman band at 815 cm^{-1} for Ag/quartz and $Ag/\alpha\text{-}Al_2O_3$ samples, which was stable up to 623 K, and also assigned this band to the O−O stretching vibration of a molecularly adsorbed oxygen species. An isotopic shift of 20 cm^{-1} upon replacing $^{16}O_2$ with $^{18}O_2$ was observed for the 815 cm^{-1} Raman band. Miller et al.[20] observed a 960 cm^{-1} Raman band on polycrystalline silver and assigned it to O_2^- species stabilized on subsurface oxygen-modified silver sites. In these three cases, the small magnitude of the isotopic shift (20−22 cm^{-1}) and the high temperatures employed may suggest that the bands at 960, 870, and 815 cm^{-1} observed by these authors actually originated from atomic oxygen species on silver. It is also hard to understand how IR vibrations in the 800−900 cm^{-1} region for the Ag/SiO_2 and $Ag/\gamma\text{-}Al_2O_3$ catalysts could be observed since both supports strongly absorb the IR radiation in this frequency range.

The Raman band at ∼956 cm^{-1} that is stable up to 580 K, was also observed on Ag(111) by Bao et al.[12] although it was not always seen in their studies. This Raman band was assigned to Ag−O vibrations of surface oxygen species[12] and was stable up to 623 K on polycrystalline silver. The isotopic shift of ∼25 cm^{-1} and absence of isotopic scrambling for this band, which is not consistent with molecularly adsorbed O_2, indicate the atomic nature of the adsorbed oxygen species. The vibration frequency of ∼956 cm^{-1} is located in the frequency range for the vibrations of metal−oxygen double bonds (M═O) in transition metal oxides and supported metal oxides are usually observed.[40] For example, the Raman stretching mode of terminal V═O groups of bulk V_2O_5 is at 997 cm^{-1} and the Raman stretching mode of Mo═O in bulk MoO_3 is at 990 cm^{-1}. Therefore, the ∼956 cm^{-1} band on silver is tentatively assigned to the stretching vibration of a surface atomic Ag═O species that is sitting on the top of an Ag atom. This atomic oxygen species seems to be relatively inactive since interaction with H_2O, C_2H_4, CO_2, and MeOH does not occur to any appreciable extent (see Figures 6−14), which is consistent with the observation that the M═O terminal bond in supported metal oxide catalysts is not the kinetically active functionality for many oxidation reactions.[41] Furthermore, the isotopic shift $\nu(^{18}O)/\nu(^{16}O)$ of 0.974 is in good agreement with the value of 0.961 measured for the V═O terminal bond in supported vanadia catalysts.[41b]

The Ag═O species in the presence of subsurface oxygen was previously proposed by van Santen et al.[5] as the active site for epoxidation of ethylene. Millar et al.[20] postulated that the band at 780 cm^{-1} is due to the Ag^{III}═O species, which is formed only on surface silver sites modified by the presence of subsurface oxygen.

Evidence from the current work unequivocally confirms that the oxygen species responsible for the Raman band at 800 cm^{-1} is a surface atomic oxygen species. The magnitude of the isotopic shift is ∼20 cm^{-1} (see Figure 5 and Table 4), which is much smaller than that typical for the O−O vibration of adsorbed molecular oxygen on silver. The presence of this oxygen species greatly enhances formation of the water-induced oxygen species responsible for the 963 and 870 cm^{-1} Raman bands when interacting with H_2O and D_2O at room temperature (compare Figures 7−9). At modest temperatures (<200 °C),

TABLE 5: Comparison of Vibration Frequencies for OH on Silver (data for OD in parentheses)

sample	Ag−OH (OD) stretch	AgO−H (O−D) bending	AgO−H (O−D) stretch	assignment	method	experimental conditions	ref
Ag(110)	280 (270)	670 (490)	3380 (2510)	surface OH	EELS	H_2O (D_2O) UHV, 255 K	[43]
Ag(111)	554	985 870	not reported	surface OH subsurface OH	Raman	$H_2O + O_2$, 300 K	[21]
Ag(111) Ag(110)	600 (558) 898 (874)		3212 (2745)		Raman	$N_2 + H_2$ (D_2), 700 K	[44]
Ag(poly) electrode	470	860	not reported	adsorbed OH	Raman	NaOH, 300 K	[49]
Ag(111) electrode	480−490 540−560	710−740 812 (560)	not reported	adsorbed OH	Raman	NaOH, 300 K NaF + NaOH	[45]

this oxygen species reacts with water-induced oxygen species and leads to complete disappearance of this oxygen species at temperatures < 200 °C, which is stable at the temperatures under flowing O_2 or He (see Figures 3 and 4). However, the Raman band at 800 cm^{-1} was still present at temperatures >200 °C when O_2 was added to the D_2O/He flowing stream (see Figure 8) since the consumed atomic oxygen by the water-induced oxygen species was repopulated from the gaseous O_2. A similar Raman band at 803 cm^{-1} was also reported by Bao and Pettinger et al.[12,42] for Ag(111) and Ag(110) and initially assigned to strongly chemisorbed atomic oxygen[42] and subsequently to a subsurface atomic oxygen.[12] The atomic oxygen species of the 803 cm^{-1} band reported by these authors is stable up to 930 K, which is much higher than that (<673 K) for the 800 cm^{-1} Raman band observed in this work.

The vibrational frequency of ∼800 cm^{-1} is located in the frequency range typically observed for the vibrations of bridging metal−oxygen bonds (M−O−M) in transition metal oxides.[40] The 800 cm^{-1} band in Bao's work[6] was found not to be present on a nonfaceted Ag(110) surface upon exposing the single-crystal sample to 20% O_2/80% N_2. However, a faceted Ag(110) surface with the local facet planes having (111) orientation and an average dimension of 500 × 1000 nm^2 exhibits an intense 800 cm^{-1} band, suggesting that the atomic oxygen species responsible for this band might sit on the interstices formed by three Ag atoms on Ag(111) surface. Thus, the atomic oxygen species associated with the 800 cm^{-1} Raman band can be designated as Ag−O−Ag, which is similar to the bridging bonds in transition metal oxides.[40]

Recent STM studies on single-crystal silver have investigated the effects of various adsorbates on silver and have found significant surface restructuring upon exposure to oxygen, chlorine, and carbon dioxide.[42b] Hashizume et al.[42c] observed the formation of −Ag−O−Ag− chains along the [001] direction on Ag[110] after exposure to oxygen at room temperature by STM and these observations are consistent with the findings in this work.

The atomic oxygen species corresponding to the 800/778 cm^{-1} band most likely sits on the silver surface since it is accessible to water, ethylene, and methanol (see Figures 6−14). The high activity of this surface atomic oxygen species is in agreement with prior findings that the bridging oxygen atoms of surface metal oxide species on oxide supports are the active sites for many oxidation reactions (e. g., methanol, alkanes, SO_2, and CO oxidation).[40]

When a gaseous stream containing H_2O or D_2O flowed over the preoxidized silver catalysts at room temperature, two new Raman bands appeared at 963 and 866 cm^{-1} in addition to the initial Raman bands at 956 and 800 cm^{-1}, which correspond to the atomic oxygen species Ag=O and Ag−O−Ag, respectively (see Figures 6−9). The small shift from 956 to 963 cm^{-1} may originate from the same oxygen species that is only mildly perturbed by the adsorption of moisture. Two new Raman bands do not exhibit isotopic shifts when H_2O is replaced with D_2O, strongly suggesting that these bands correspond to oxygen species and not OH species. The vibrational frequencies reported in the literature for OH species on Ag surfaces, compared with the data for OD species, are summarized in Table 5. Considerable variations of vibrational frequencies were observed for the Ag−OH stretching, AgO−H bending, and AgO−H stretching modes upon deuteration. Typical values of νH/νD are ∼1.34 for the AgO−H stretching and bending vibrations and ∼1.04 for the Ag−OH stretching vibration, respectively.[43−46] Itoh et al.[47] demonstrated that the strong Raman bands at 500, 800, and 900 cm^{-1} over a silver electrode in 0.5 M alkali-hydroxide aqueous solutions were associated with the existence of atomic oxygen species adsorbed on the silver electrode instead of surface hydroxide species based on the observation that there was no isotope effect. The oxygen species responsible for the bands 963 and 866 cm^{-1} may form through dissociation of adsorbed water. Kurina et al.[48] demonstrated that water could dissociatively adsorb on both clean and preoxidized polycrystalline silver surfaces at temperatures of 300−600 K to form a surface OH species using TPD and adsorption kinetic measurements. The water-induced oxygen species could react with the surface atomic oxygen responsible for the 800 cm^{-1} band at temperatures lower than 473 K (see Figures 6 and 7), further suggesting the atomic nature of the oxygen species responsible for the 866 cm^{-1}.

TABLE 6: Raman Assignments from This Work

vibrational frequency (cm^{-1})	assignments
956−963	Ag=O, surface
866	Ag−O−Ag, surface
800	Ag−O−Ag, surface
620	Ag−O, bulk

Iwasaki et al.[49] assigned a band at 860 cm^{-1}, which was observed in a wider electrode potential range, to the bending vibration of the adsorbed hydroxyl species. The Raman band at ∼870 cm^{-1} was also reported on Ag(111) as well as a silver electrode and was assigned to the bending vibration of subsurface and adsorbed OH groups.[21,26] The assignments in these two cases are questionable due to lack of isotopic data to support the assignments.

A summary of the observed Raman bands and their assignments in this investigation are given in Table 6. The 620 cm^{-1} band was not observed in our in situ Raman studies where the highest temperature was only allowed to reach 500 °C due to the in situ cell design. However, the 620 cm^{-1} band was always present in the ambient Raman spectra after the silver samples were calcined at 550 °C for 2 h. Thus, it appeared that the bulk oxygen species responsible for the 620 cm^{-1} band formed at temperatures higher than 500 °C in an oxygen environment.

Active Sites for Ethylene Oxidation. The present in situ Raman studies demonstrate that interaction of ethylene with preoxidized silver surface causes considerable diminishment of the surface atomic oxygen species associated with the 800 cm^{-1} Raman band. The atomic oxygen species associated with the 956 cm^{-1} band does not appear to significantly interact with the ethylene molecules. Furthermore, isotopic studies showed that the 931 cm^{-1} band due to $Ag{=}^{18}O$ species was very stable compared to the 778 cm^{-1} band due to $Ag{-}^{18}O{-}Ag$ under ethylene oxidation conditions using $^{16}O_2$ as oxidant. Similar observations were also made in this study with alumina-supported silver catalysts that were preoxidized at high temperatures (the results are not shown here).

Bao et al.,[12] Kondarides et al.,[18] and Boghosian et al.[50] have also indicated that ethylene interacts with the oxygen species corresponding to the Raman band at ~800 cm^{-1}, despite different assignments for this band. Millar et al.[20] have postulated that the ethylene epoxidation reaction occurs on an Ag^I site modified by subsurface oxygen, which is responsible for a Raman band at 780 cm^{-1}, because of the inaccessibility of ethylene to the subsurface atomic oxygen species.

Kondarides et al.[18] concluded that the oxygen species responsible for the 815 cm^{-1} band was not a catalytically active site for ethylene oxidation because of the slow variation in the 815 cm^{-1} band with time upon changing the reactant gaseous composition. The 815 cm^{-1} Raman band was assigned by Kondarides et al. to the ν (O−O) stretching vibration of a molecular species on oxide-supported silver catalysts. However, Kondarides et al. reached this conclusion without considering the migration of dissolved bulk oxygen species to the silver surface sites during ethylene oxidation. It is a very important characteristic feature of the oxygen−silver systems that dissolved atomic oxygen species can migrate and repopulate the surface atomic oxygen species.[12]

Active Sites for Methanol Oxidation. The current in situ Raman spectroscopic experiments demonstrate that the surface atomic oxygen species (Ag−O−Ag) plays an important role in methanol oxidation over silver. Exposure of silver to the methanol oxidation reaction environment at 250 °C resulted in significant diminishment of the 800 cm^{-1} Raman band, but not the 956 cm^{-1} band (see Figure 14a,b). Elevation of the reaction temperature to 350−500 °C (see Figure 14c−e) caused substantial changes in the Raman bands. The very broad and weak feature in the ~720−870 cm^{-1} region indicates the concurrent presence of several different oxygen species. The 800 and 870 cm^{-1} Raman bands have already been assigned to the surface atomic oxygen species in this work. The 870 cm^{-1} band is present when flowing water or deuterium oxide over preoxidized silver and, thus, this band may be induced by the product water or the reactant methanol. The vibrational frequencies of these oxygen-related species are located in the frequency range for the vibration of bridging M−O−M bonds in transition metal oxides.[40] It was found that the atomic oxygen species responsible for the 800−870 cm^{-1} bands were greatly stabilized by the methanol oxidation reactant steam in comparison to the environments of flowing He or O_2 (see Figures 3 and 4). This effect was not observed for the Ag═O atomic oxygen species corresponding to the 956 cm^{-1} Raman band, which completely desorbed at temperatures above 350 °C during methanol oxidation. Thus the Ag═O atomic oxygen species are not the oxygen species responsible for methanol oxidation under industrial conditions.

The conclusions drawn from this work are in good agreement with the previous work conducted by Wachs and Madix.[2] Wachs et al. demonstrated that surface oxygen atoms on silver facilitates the dissociative chemisorption of methanol on the Ag(110) surface as CH_3O, which subsequently decomposes to produce formaldehyde. Furthermore, the conclusions from this work is also consistent with the results for methanol oxidation over supported metal oxide catalysts, where it was concluded that the bridging M−O−M bond is the active functionality and the terminal M═O bond is inactive for methanol oxidation.[40]

Wachs and Madix[2] demonstrated that the presence of excess surface oxygen on single-crystal Ag(110) leads to the further oxidation of adsorbed H_2CO to carbon dioxide and water. The catalytic data in a fixed-bed reactor (Table 3) clearly indicated that when the MeOH/O_2 molar ratio decreases from 3.08 to 0.95, the selectivity to formaldehyde significantly diminishes from 92.3 to 69.1%, and the selectivity to carbon dioxide drastically increases from ~7 to ~31%. It was also found that the very broad Raman feature at ~870 cm^{-1} became very strong when the MeOH/O_2 molar ratio decreased to 0.48 (not shown here). Bao et al.[21] also observed very intense 800 cm^{-1} as well as 870 cm^{-1} bands upon addition of methanol (200 mbar) to the O_2 stream (800 mbar) since a large amount of excess O_2 was employed in their work.

Recently, it was shown that silver surfaces undergo restructuring and pinhole formation under methanol oxidation conditions as demonstrated by SEM and STM studies.[42b,51,52] The pinhole formation was proposed to occur as a result of reaction between dissolved hydroxyl groups and the formation of water, which resulted in hydrostatic pressure to adopt a “hill and valley” conformation in order to minimize the surface free energy. Based on this, Millar et al.[52] suggested that methanol reacted with subsurface oxygen, which is the active species for methanol oxidation, to produce subsurface hydroxyl species that formed water in the subsurface layers. However, subsurface hydroxyls could alternatively form through diffusion of hydrogen atoms combining with bulk oxygen species since the small hydrogen atoms can readily diffuse into the silver bulk at reaction conditions. Methanol needs to directly contact with the active oxygen species and to form intermediate surface methoxy species and, thus, surface atomic oxygen species are the best candidates to physically fulfill the oxidation reaction.

It is important to put in situ Raman studies in perspective to industrial selective oxidation reactions over silver catalysts and UHV surface science studies that have appeared in recent years. A unique feature of in situ Raman investigation is that silver catalysts are preoxidized at elevated temperatures in order to produce roughened silver surfaces that give rise to surface-enhanced Raman (SERS) signals. In the case of methanol oxidation, a preoxidized silver surface initially results in a more active catalyst, but after several hours the same steady-state is reached with or without the preoxidation treatment.[53] This situation occurs because the net reducing environment typically employed during methanol oxidation, molar ratio of CH_3OH/O_2 ~3 as well as the production of significant amounts of H_2 byproduct, results in a silver surface that is essentially reduced and contains only trace amounts of adsorbed atomic oxygen under steady-state conditions (see Figure 14). Thus, methanol oxidation readily proceeds over preoxidized as well as reduced silver surfaces and that the above in situ Raman studies and the UHV surface science studies[2] provide fundamental information that is directly relevant to the industrial oxidation of methanol over silver catalysts. In the case of ethylene oxidation, the commercial catalysts consist of silver particles supported on a low surface area α-alumina support and high-temperature preoxidation is not desirable since it will cause sintering of the silver particles. Furthermore, the high C_2H_4/O_2 ratios and elevated temperatures employed in industrial conditions probably result in a silver surface that is only mildly preoxidized or even reduced. These conditions should be close to those under UHV surface science studies. The surface science studies have nicely demonstrated that molecularly adsorbed oxygen is present only at low temperatures and does not react with ethylene prior to oxygen desorption.[54] Furthermore, these fundamental studies have also shown that only specific adsorbed atomic oxygen species react with ethylene.[54] Although the in situ Raman studies above involved preoxidized silver studies, they demonstrated that adsorbed molecular oxygen is not present on the silver surface at conditions employed for ethylene oxidation and that only specific adsorbed atomic oxygen species, Ag−O−Ag corresponding to the Raman band ~800 cm^{-1}, are involved in the ethylene oxidation reaction. Thus, it appears that both the in situ Raman studies and the UHV surface studies have provided many fundamental insights into the industrial selective oxidation reactions over silver catalysts.

Conclusions

In situ Raman spectra were obtained during the interaction of polycrystalline silver with oxygen, water, carbon dioxide, ethylene, and methanol at atmospheric pressure and temperatures between 25 and 500 °C. Upon exposure to $^{16}O_2$, two Raman bands related to oxygen species were observed at 956 and 800 cm^{-1}, which shifted to 931 and 778 cm^{-1} upon replacement of $^{16}O_2$ with $^{18}O_2$. The 956 cm^{-1} band is assigned to the stretching vibration of a surface atomic oxygen sitting on the top of a Ag atom with a Ag═O double bond, stable up to 250 °C, and does not appear to interact with water, ethylene, and methanol. The 800 cm^{-1} Raman band is assigned to the stretching vibration of a surface atomic oxygen species sitting on the interstices of three Ag atoms with Ag−O−Ag bonds, stable up to 300 °C, and readily interacts with water, ethylene, and methanol. Upon exposure of preoxidized silver to H_2O and D_2O, two new Raman bands appear at 963 and 866 cm^{-1}, which are also assigned to surface atomic oxygen species because of the absence of an isotopic shift when H_2O is replaced with D_2O. This work suggests that the Ag−O−Ag surface atomic oxygen species corresponding to the 800 cm^{-1} band is involved in ethylene and methanol oxidation over silver catalysts. During methanol oxidation, excess oxygen populates the surface atomic oxygen species responsible for the 866 cm^{-1} band, which appears to be involved in the further oxidation of H_2CO to CO_2.

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