NMR Study of Species Formed during Ethylene Oxidation over Supported Silver

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^{13}C solid-state NMR spectroscopy has been used to study the various species formed during the oxidation of ethylene on Ag catalysts. The NMR spectra obtained after heat treatments of sealed catalyst samples provide direct observation of surface species which can be identified by their chemical shift values. This study also reports ^{13}C shifts for standard compounds dispersed on $Ag/\eta\text{-}Al_2O_3$ and Ag/SiO_2 which provide groups that can be present under reaction conditions, and the decomposition of ^{13}C-labeled ethylene oxide on Ag/SiO_2 in the absence of O_2 was investigated. On the basis of these experiments, ^{13}C assignments have been made for the following adsorbed species: ethylene oxide, formic acid, formate, oxalic acid, oxalate, acetic anhydride, acetaldehyde, and carbonate. In the absence of O_2, ethylene oxide decomposed to acetic acid, acetaldehyde, and formaldehyde, and broad peaks indicative of polymers on the SiO_2 surface were also observed. The observation of ethylene oxide adsorbed on Ag/SiO_2 after reaction between $^{13}C_2H_4$ and O_2 was consistent with a previous study showing this catalyst was much more selective than a $Ag/\eta\text{-}Al_2O_3$ catalyst; CO_2, adsorbed $^{13}C_2H_4$, and a deprotonated oxalate or formate species were also identified. The formation of CO_2 in the absence of aldehyde or acetate species but in the presence of oxalate species suggests an alternative route may exist for complete oxidation that does not involve isomerization of ethylene oxide.

Introduction

Many studies have been devoted to the epoxidation of ethylene to ethylene oxide over silver catalysts, and most of them have been summarized in various reviews.[1-5] Yet despite numerous investigations of the kinetics of ethylene oxidation and the nature of the various species formed on the catalyst under reaction conditions, a complete understanding of the mechanisms for the epoxidation and combustion reactions does not currently exist. The primary technique to characterize the adsorbed species on the catalyst has been infrared spectroscopy;[6-10] only two papers in the open literature have utilized nuclear magnetic resonance (NMR) to identify species formed from C_2H_4 and O_2 over Ag catalysts.[11,12] NMR provides a means by which reaction intermediates and products can be observed directly when labeled compounds coupled with techniques such as cross-polarization with magic-angle spinning (CPMAS) are used to enhance the NMR signal.[13] The present work was undertaken to try to unambiguously identify the various intermediates formed on a silver catalyst surface during the oxidation of ethylene by the direct comparison of ^{13}C spectra obtained from standards adsorbed on the catalyst surface with spectra obtained from ^{13}C-labeled ethylene after reaction with oxygen. In the previous NMR studies of this reaction, there has been uncertainty about some of the chemical shift assignments, especially in the carbonyl region of the spectrum. Because interactions of the adsorbed species with the support or metal can significantly change their chemical shifts, it is necessary to obtain spectra of standard species adsorbed on the appropriate catalyst or support system. This information is vital for a better understanding of the surface reactions that can occur.

The standards chosen for this study contained chemical groups that represent intermediates that could be formed on the basis of the mechanisms proposed for the epoxidation and combustion reactions of ethylene. The ^{13}C chemical shifts obtained for the standards are compared with those observed for the actual reaction products and intermediates both in this work and in earlier NMR studies. The two silver catalyst systems studied here are $Ag/\eta\text{-}Al_2O_3$ and Ag/SiO_2. Plischke *et al.* have previously reported an investigation in which a pretreated $Ag/\eta\text{-}Al_2O_3$ catalyst was exposed to isotopically enriched $^{13}C_2H_4$ at room temperature and sealed in glass ampules for ^{13}C NMR.[11] The NMR spectra revealed a variety of species, only some of which were conclusively identified. The present work includes a similar study carried out on a Ag/SiO_2 catalyst which is known to have better selectivity for the epoxidation of ethylene than the $Ag/\eta\text{-}Al_2O_3$ catalyst examined earlier.[14] The intermediates and products formed were characterized with ^{13}C NMR by using single-pulse Bloch decay, CPMAS, and dipolar dephasing experiments. The chemical shifts for carbonate, anhydride, formate, and oxalate species on these two catalysts have been unambiguously determined, and in combination with other known shifts, an effort was made to better understand the surface chemistry occurring on silver catalysts by using NMR spectra obtained after incremental heat treatments of catalysts sealed under ethylene and oxygen. In addition, a study of ethylene oxide (EO) on a Ag/SiO_2 catalyst was carried out. The impact of these results on the reaction pathway is discussed.

Experimental Section

Catalyst Preparation and Characterization. A 2.8 wt % Ag/SiO_2 catalyst and a 0.7% Ag/SiO_2 catalyst were prepared by an ion-exchange technique similar to that outlined by Benesi *et al.*[15] A silver amine complex was prepared in deionized, distilled water from silver nitrate (Fisher, 99.999%) and ammonium hydroxide. The pH of the mixture was adjusted to 9 with the latter, and the mixture was added dropwise to a stirred slurry of silica (Davison, grade 57, 220 m^2/g) in water. After stirring for 30 min to ensure uniform dispersion, the mixture was filtered, washed, dried overnight at 373 K, and then stored in a desiccator. The 5% $Ag/\eta\text{-}Al_2O_3$ catalyst was previously prepared by Plischke.[16] The Ag loading was determined by atomic absorption spectroscopy in the Mineral Constitution Laboratory at The Pennsylvania State University.

The catalyst pretreatment procedure involved calcination under a flowing mixture of 10% O_2 in He at 773 K for 2 h followed by

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reduction at 673 K for 2.5 h under flowing H_2, and it has been outlined in detail elsewhere.[16] Oxygen adsorption was determined at 443 K, and ethylene adsorption was measured at room temperature. All gases used were ultrahigh purity (MG Industries, 99.999%) except for ethylene (MG Industries, 99.5%). The catalyst sample was placed in a Pyrex cell which allowed flowing gas to be used during pretreatment. For the sealed samples required for NMR, specially prepared closed-end cells (Wilmad) with a constriction 1 cm from the bottom were used. In this case, the pretreatments were carried out under nonflowing conditions in which the gas was evacuated and replaced with fresh gas every half hour. Both types of cells were attached via FETFE O-ring joints to the adsorption apparatus. The stainless steel adsorption system utilized an Edwards Diffstak diffusion pump and has been described elsewhere.[17]

The amount of the 2.8% Ag/SiO_2 samples prepared for NMR that could fit into the specially designed cell was about 50 mg, and the constriction was flame-sealed after ethylene (1,2-$^{13}C_2$, 99%, MSD Isotopes) adsorption to yield a glass ampule that would fit into a 7-mm zirconia rotor. With one sample, after oxygen adsorption was completed the irreversibly chemisorbed oxygen was left along with a residual pressure of about 16 Torr of O_2. The ^{13}C-labeled ethylene was then rapidly introduced until the total pressure in the cell was 43 Torr. The sample was closed off, removed from the adsorption apparatus, and cooled in liquid N_2 prior to and during the sealing process (to minimize exposure to high temperatures); hence, an accurate measurement of the pressures of O_2 and C_2H_4 within the ampule could not be obtained. Preparation of another sample of the same catalyst was similar in all respects except that the O_2 was evacuated and only irreversibly adsorbed oxygen on the Ag was present prior to the addition of 19 Torr of labeled ethylene.

Preparation of Catalysts with ^{13}C-Labelled Standards. ^{13}C standards of formic acid (CIL, 99% ^{13}C), acetaldehyde (CIL, 99% 1,2-$^{13}C_2$), acetic anhydride (CIL, 99%, 1,1′-$^{13}C_2$), oxalic acid (CIL 99%, 1,2-$^{13}C_2$), and sodium carbonate (CIL, 99% ^{13}C) were prepared at various concentrations that would allow their detection but still retain the low levels that would be comparable to those obtained on the catalyst surface under the experimental conditions used. The standards were placed on both the 5% Ag/η-Al_2O_3 and the 0.7% Ag/SiO_2 catalyst and, in certain cases, also on the η-Al_2O_3 or SiO_2 support to see if any differences could be observed. Solutions of the standards were prepared in appropriate solvents, and the necessary amounts were transferred onto each sample by an incipient wetness method.[11,16] No special precautions were taken to keep the catalysts from air exposure prior to impregnation; hence it was assumed that the Ag surfaces were essentially covered by oxygen. A standard sample of ^{13}C-dilabeled ethylene oxide (Isotec, 99% $^{13}C_2$, 0.1% hydroquinone as stabilizer) on 2.8% Ag/SiO_2 was also prepared but under controlled conditions similar to those for ^{13}C-labeled ethylene. The EO was adsorbed on 50 mg of the reduced catalyst, and the ampule containing the sample was sealed off with an overpressure of EO present, as described earlier.

NMR Equipment and Techniques. All of the NMR spectra were obtained at 300 K on a CMX-300 (Chemagnetics) spectrometer operating in the quadrature mode at 74.78 MHz for ^{13}C. Proton-decoupled Bloch decay, CPMAS, and CPID experiments were used to characterize sealed samples of ^{13}C-labeled ethylene on 2.8% Ag/SiO_2, whereas the CPID technique was omitted for the analysis of the standards. The spinning speeds were about 3.5 kHz. The rf field strength for both ^1H and ^{13}C was 50 kHz.

The ^{13}C chemical shifts are reported relative to TMS, and the TMS resonance was determined from the shift of the aromatic resonance of HMB (132.2 ppm). In the Bloch decay experiments for $^{13}C_2H_4$ on the 2.8% Ag/SiO_2 catalyst, the relaxation delay used between scans was 1 s. For the corresponding cross-polarization experiments, a delay of 2 s with an optimum contact time of 1.5 ms was used. Previous work indicated that these delays are sufficient for NMR ^{13}C spin lattice relaxation of surface species.[11] For the CPID experiments, a dipolar dephasing time of 50 μs was used. For the study with the standards, fewer scans were necessary, and the relaxation delays and cross-polarization contact times vary in some cases. Due to a large, broad signal arising in both the Bloch decay and CPMAS spectra from the stator and rotor end-cap materials, it was necessary to obtain rotor "blank" spectra close in time and run under identical conditions to the samples. The appropriate blank free induction decays (FIDs) were subtracted from the sample FIDs before the signal was Fourier transformed to yield the difference spectra shown in the figures. In some cases the difference FID was left-shifted to reduce residual base-line roll from imperfect cancellation.

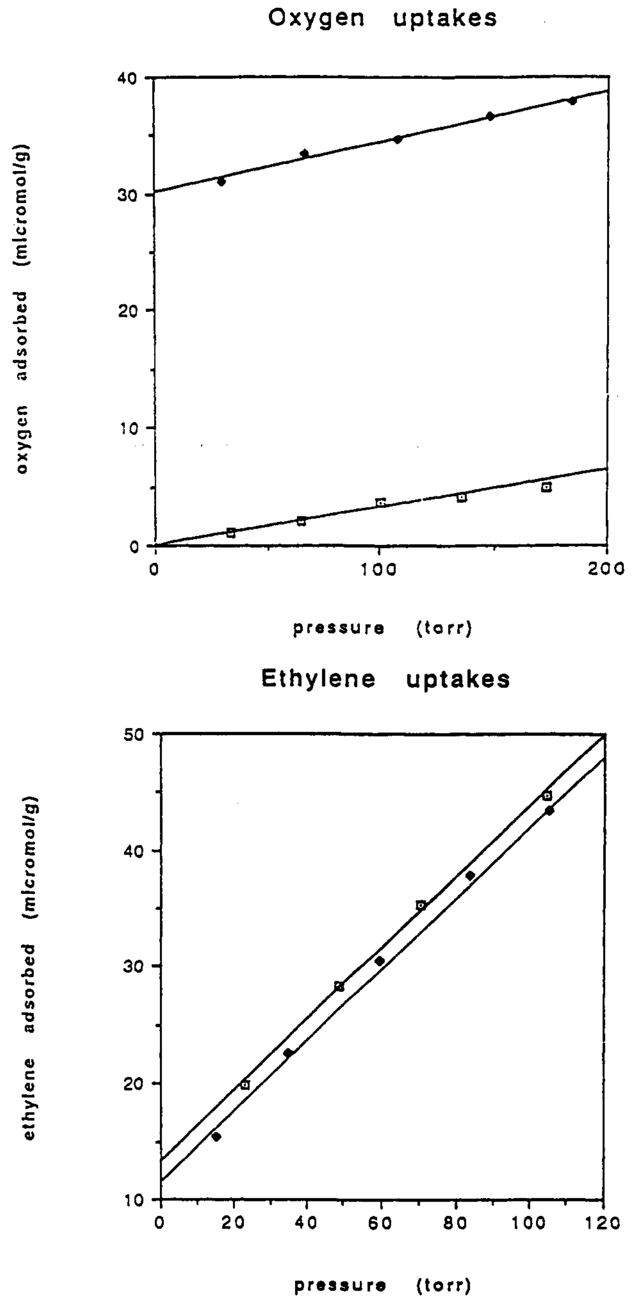

Figure 1. (a) Oxygen adsorption isotherms at 443 K for 2.8% Ag/SiO_2 (◆, total uptake; ⊡, reversible uptake) and (b) ethylene adsorption isotherms at 300 K for 2.8% Ag/SiO_2. (⊡, total uptake, ◆, reversible uptake).

TABLE 1: Gas Uptakes on 2.8% Ag/SiO$_2$^{a}

oxygen at 443 K (μmol/g cat)	ethylene at 300 K (μmol/g cat)		
irrev O$_2$ ads	C$_2$H$_4$ tot	C$_2$H$_4$ rev	C$_2$H$_4$ irrev
30.1	13.2	11.4	1.8

[a] Dispersion = O$_{ad}$/Ag$_{total}$ = 0.23. Average Ag crystallite size = 5.8 nm.

Results

Reversible and irreversible uptakes of O_2 and C_2H_4 on the 2.8% Ag/SiO$_2$ catalyst were determined from the isotherms shown in Figure 1, parts a and b, which were measured after pretreatment with flowing gases. For oxygen, only irreversible adsorption occurs on the Ag surface, which yields monolayer coverage on Ag at these conditions.[17] The initial C_2H_4 uptake is designated by C_2H_4 tot, while C_2H_4 rev represents the reversible uptake obtained after evacuation at 300 K for about 22 h. The results are presented in Table 1.

The NMR spectra for the adsorbed ^{13}C-labeled standards are presented in Figure 2, and the carbonyl chemical shifts are reported in Table 2. The NMR spectra and results for the ^{13}C-labeled EO require a more elaborate description, and hence these results are not included in Figure 2 and Table 2. The chemical shifts obtained from the previous studies[11,12] are shown in Table 3 along with the ^{13}C shifts of some compounds in the pure solid or liquid states and the shifts obtained in the present work. The downfield region between 155 and 220 ppm covers the carbonyl region. Accurate assignments must be made in this region to provide meaningful information about the nature of the products and intermediates formed during ethylene oxidation.

The ^{13}C NMR techniques used to identify the species adsorbed on the catalyst surface were Bloch decay, cross-polarization with magic-angle spinning (CPMAS), and CPMAS with interrupted decoupling (CPID). Cross-polarization enhances the observed signal for the ^{13}C spins by transfer of magnetization from the more polarized ^{1}H spins, and sensitivity is further improved by the use of ^{13}C-enriched ethylene. Unfortunately, cross-polarization is ineffective for ^{13}C nuclei that are far (>5 Å) from protons or for molecules in the liquid or gaseous state, but Bloch decay experiments yield signals for such species. The CPID or dipolar dephasing experiment is similar to the CPMAS experiment except for the introduction of a delay between cross-polarization and acquisition, during which the carbons with nearby protons undergo dephasing due to the ^{13}C–^{1}H dipolar coupling. As a result, resonances from protonated ^{13}C nuclei do not survive the delay unless there is relative motion of the nuclei which reduces the effective dipolar coupling. Examples of the latter include methyl groups and protonated carbons in molecules that are not rigidly bound to the catalyst surface. Figure 3 shows the Bloch decay, CPMAS, and CPID spectra for the Ag/SiO$_2$ catalyst after sealing with $^{13}C_2H_4$ and O_2 and prior to any heat treatments.

TABLE 2: Carbonyl Chemical Shifts Obtained for Standard Compounds (ppm, Relative to TMS)

standard	loading (wt %)	impregnation solvent	system	chemical shift (ppm)
formic acid	0.8	acetone	5% Ag/Al$_2$O$_3$	170
	0.5	acetone	η-Al$_2$O$_3$	168
	0.05	acetone	η-Al$_2$O$_3$	165
	0.05	acetone	5% Ag/Al$_2$O$_3$	165
	0.08	acetone	0.7% Ag/SiO$_2$	172
	0.04	acetone	0.7% Ag/SiO$_2$	172
	0.04	acetone	SiO$_2$	174
sodium formate	0.03	acetone–water	SiO$_2$	172
acetic anhydride	0.05	chloroform	5% Ag/Al$_2$O$_3$	183
	0.05	chloroform	0.7% Ag/SiO$_2$	183
	0.05	chloroform	SiO$_2$	179
oxalic acid	0.2	water	5% Ag/Al$_2$O$_3$	167
	0.2	water	0.7% Ag/SiO$_2$	168
	100			161, 163, 165, 167
sodium oxalate	0.2	water	SiO$_2$	169
sodium carbonate	0.2	water	5% Ag/Al$_2$O$_3$	167
	0.2	water	0.7% Ag/SiO$_2$	172
	100			171
acetaldehyde	7	water	5% Ag/Al$_2$O$_3$	206
	10	water	0.7% Ag/SiO$_2$	207

Figures 4, 5, and 6 show the room temperature NMR spectra obtained with Bloch decay, CPMAS, and CPID experiments, respectively, after the sample had been heated to increasingly

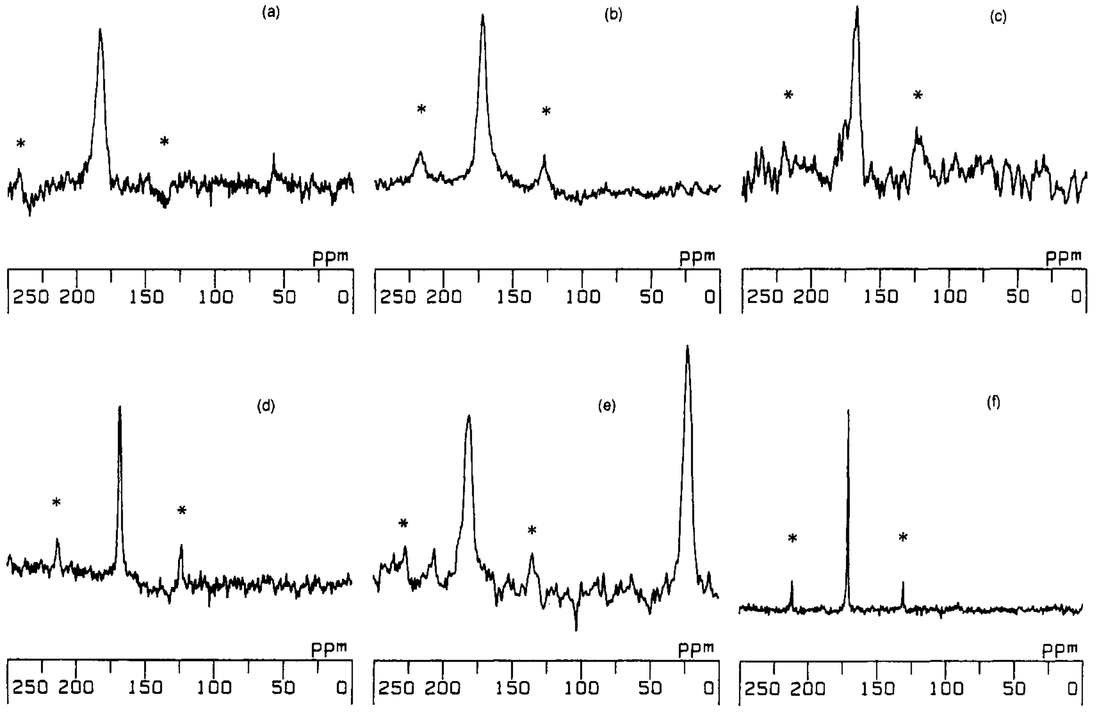

Figure 2. (a) CPMAS spectrum of 0.05% [1,1-^{13}C]acetic anhydride on Ag/SiO$_2$ (b) CPMAS spectrum of 0.08% [^{13}C]formic acid on Ag/SiO$_2$, (c) CPMAS spectrum of 0.2% [1,2-^{13}C]oxalic acid on Ag/Al$_2$O$_3$, (d) CPMAS spectrum of 0.2% [1,2-^{13}C]oxalic acid on Ag/SiO$_2$, (e) CPMAS spectrum of 7% [1,2-^{13}C]acetaldehyde on Ag/Al$_2$O$_3$, and (f) Bloch decay spectrum of pure [^{13}C]Na$_2$CO$_3$. Spinning sidebands are denoted by asterisks.

TABLE 3: Comparison of Chemical Shift Assignments (ppm, from TMS)

	after C_2H_4 reacts with oxygen on catalyst			standard compounds, this study		
compound	Ag/SiO_2 (ref 12)	Ag/η-Al_2O_3 (ref 11)	Ag/SiO_2 (this study)	on Ag/SiO_2	on Ag/Al_2O_3	pure liq or solid
acetaldehyde				207, 20	206, 23	200, 31[c]
acetic acid	177, 17					176, 20[c]
Ag acetate		179,19				179, 19[a]
formic acid				172	165	166[b]
formate		164	164	172		171[b]
anhydride	183			179	183	167[c]
carbonate		170		171–172	167	171[d]
oxalic acid				168	167	161–167[d]
oxalate		159	164	169	167	161–167[d]
CO_2	124	126	126			124[b]
alkoxy	65, 25	61, 28	64, 30			
ethylene	119–123	103–124	111–124			123[c]
ethylene oxide	40		47	41		41[c]
ethane	5		5[e]			6[c]
CH_3CH_2COOH	8, 29, 183					
$SiO(CH_2)_2OH$	64		64			

[a] From ref 11. [b] From ref 18. [c] From ref 19. [d] This study. [e] Observed with $^{13}C_2H_4$ on Ag/SiO_2 (irreversibly adsorbed oxygen only).

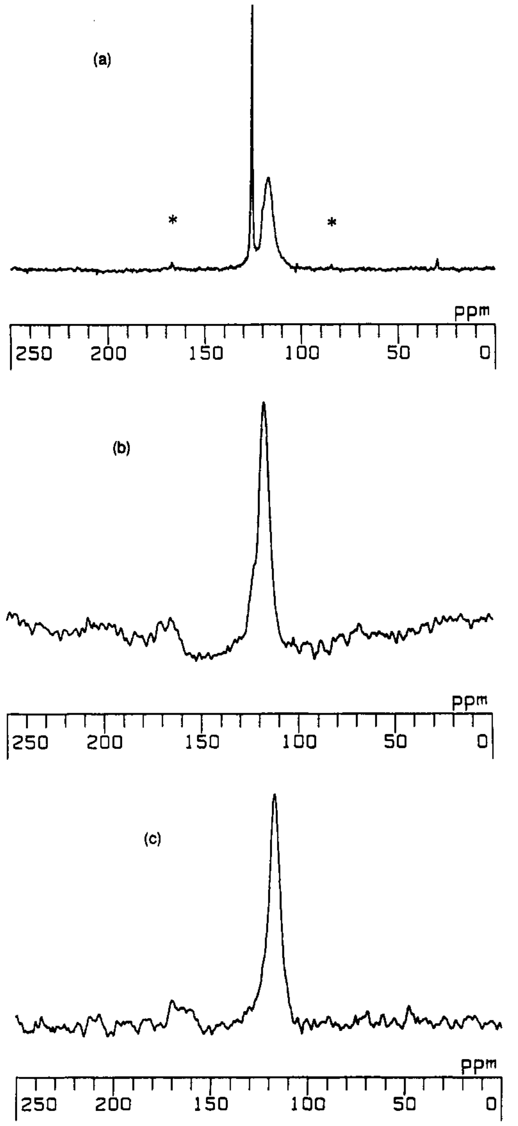

Figure 3. NMR spectra of [^{13}C]ethylene with O_2 on 2.8% Ag/SiO_2 at 300 K (prior to heat treatments): (a) Bloch decay spectrum, (b) CPMAS spectrum, and (c) CPID spectrum. Spinning sidebands are denoted by asterisks.

higher temperature; that is, the sample was treated at each indicated temperature for 15 min followed by a subsequent room temperature NMR experiment. Only the region between 250 and 0 ppm is exhibited since no resonances outside of this region were observed. All spectra obtained in Figures 3, 4, 5, and 6 were obtained under identical conditions with the same number of transients (36 000). In all cases, the background ^{13}C signal from the rotor end-caps and stator has been subtracted, as described in the Experimental Section. An artifact at 102–103 ppm corresponding to the carrier frequency is seen in many of the spectra, as is a residual base-line roll due to imperfect subtraction of the ^{13}C background signal.

The Bloch decay spectrum at 300 K (Figure 3a) reveals the presence of peaks at 30 and 126 ppm in addition to a broad resonance centered between 115 and 120 ppm. The corresponding CPMAS and CPID spectra (Figure 3b,c) contain the same broad resonance centered about 117 ppm. A weak signal also appears to exist in the region between 160 and 170 ppm. The only change in the Bloch decay spectrum after 15 min of heating at 373 K (Figure 4a) is the disappearance of the resonance at 30 ppm. The corresponding CPMAS spectrum (Figure 5a) shows the same large broad resonance centered at 117 ppm and a broad downfield signal between 160 and 170 ppm; in addition, a peak at 47 ppm is present that is not observed in the Bloch decay spectrum. Heat treatment at 448 K produces more changes, with the peak at 47 ppm now visible in the Bloch decay spectrum, a considerable decrease in the broad resonance which has shifted slightly to 118 ppm, and an increase in the 126 ppm peak. CPMAS once again does not show the peak at 126 ppm, which is the most prominent peak seen in the Bloch decay spectrum, but gives a more intense signal than before for the resonance at 47 ppm. In addition, the broad signal between 160 and 170 ppm has resolved to give a sharper peak at 164 ppm. Heat treatment at 503 K produces further changes in the Bloch decay spectrum: A new sharp resonance appears at 123 ppm, there is an upfield shift to 111 ppm of the broad resonance, which has decreased even further, and there is a decrease in intensity for the resonance at 47 ppm. The CPMAS spectrum still shows the peak at 47 ppm quite clearly in addition to resonances at 123 and 164 ppm. After heating to 573 K the Bloch decay spectrum shows that the signal at 126 ppm has noticeably increased, the broad resonance at 111 ppm remains the same, and the sharp peaks at 123 and 47 ppm have now disappeared. An additional broad resonance barely discernible at 64 ppm has formed. The CPMAS spectra show all three signals survive the heat treatments up to 573 K. The CPID spectra (Figure 6) show that only two of the three major resonances seen in the CPMAS spectrum survive the dipolar dephasing with significant signal to noise, although the third resonance at 164 ppm may be obscured by residual base-line roll. It is noteworthy that the upfield resonance at 47 ppm is weaker and has disappeared from the CPID spectrum after heat treatment at 573 K.

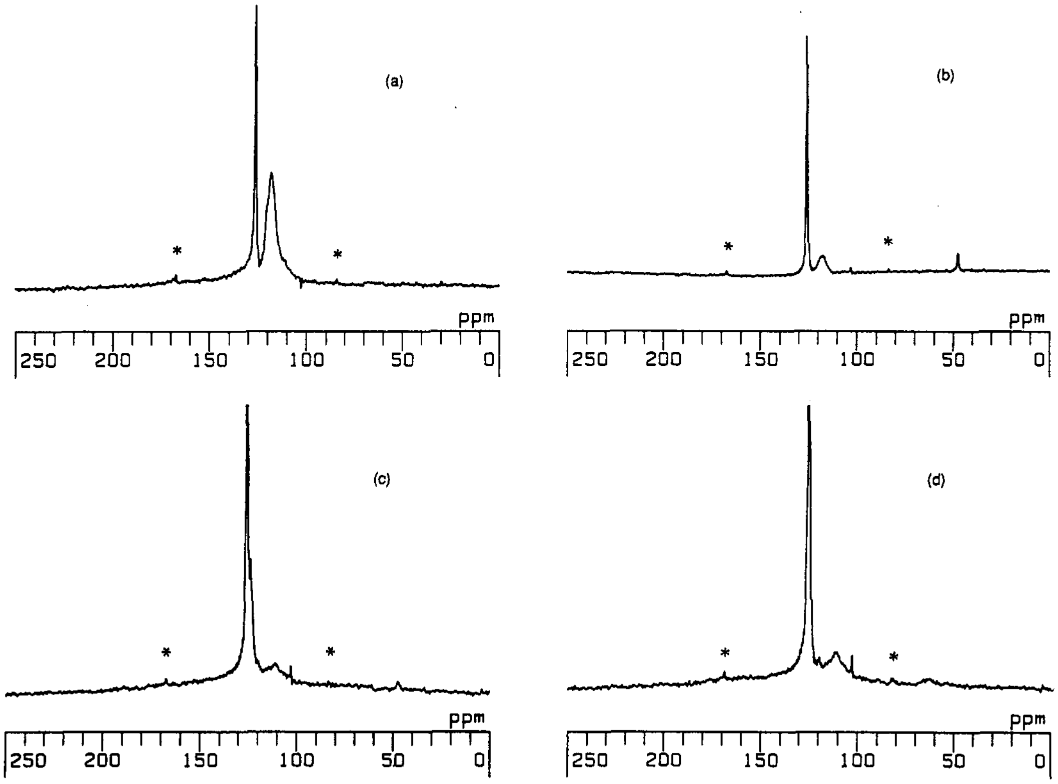

Figure 4. Bloch decay spectra at 300 K after heat treatments of C_2H_4 and O_2 over 2.8% Ag/SiO_2 at (a) 373, (b) 448, (c) 503, and (d) 573 K. Spinning sidebands are denoted by asterisks.

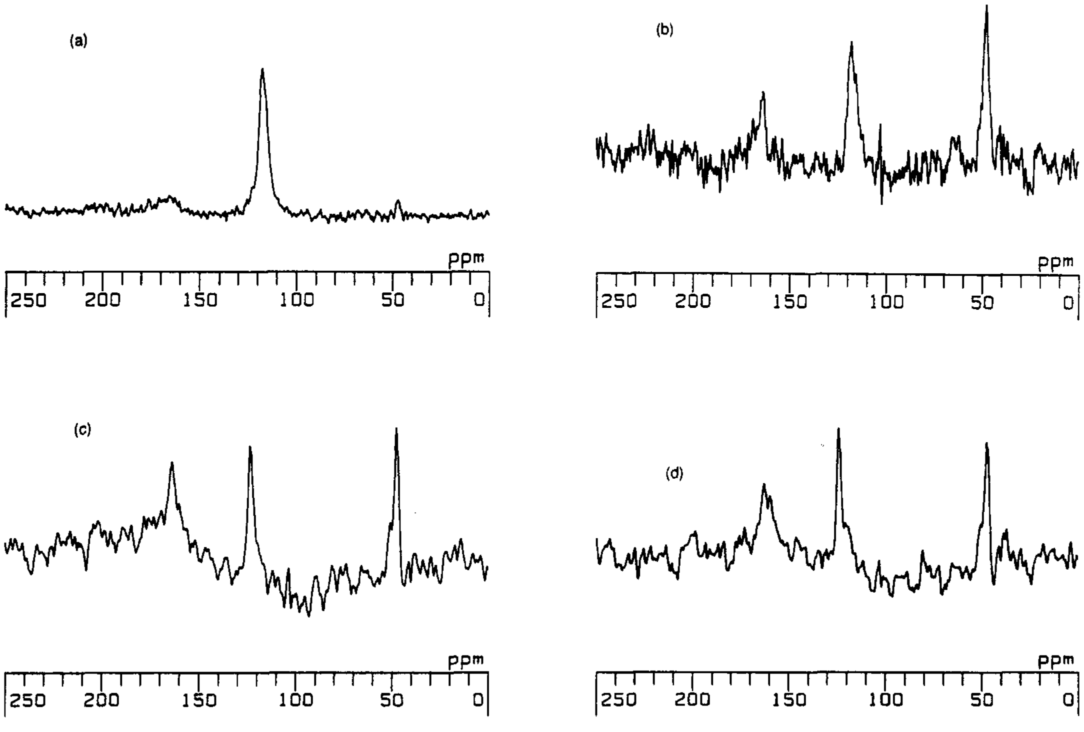

Figure 5. CPMAS spectra at 300 K after heat treatments of C_2H_4 and O_2 over 2.8% Ag/SiO_2 at (a) 373, (b) 448, (c) 503, and (d) 573 K.

Figure 7 shows the background-corrected Bloch decay and CPMAS spectra obtained after heating to 623 K a 2.8% Ag/SiO_2 catalyst sample which contained *only irreversibly adsorbed oxygen* prior to the introduction of the labeled ethylene. Both spectra reveal a sharp resonance at 122 ppm, and the Bloch decay spectrum shows an additional small peak around 5 ppm. Prior spectra obtained after heat treatment at lower temperatures provided no new information other than the expected trend of narrowing line width for the peak at 121 ppm with increasing temperature.

Figures 8 and 9 show the Bloch decay spectra and CPMAS spectra, respectively, for ^{13}C-labeled EO on reduced 2.8% Ag/SiO_2, taken at room temperature and after heat treatments at 373, 423, and 473 K. The following resonances are observed: a sharp peak at 41 ppm, seen clearly in the spectra prior to heat treatment at 423 K; intense broad peaks in the region between

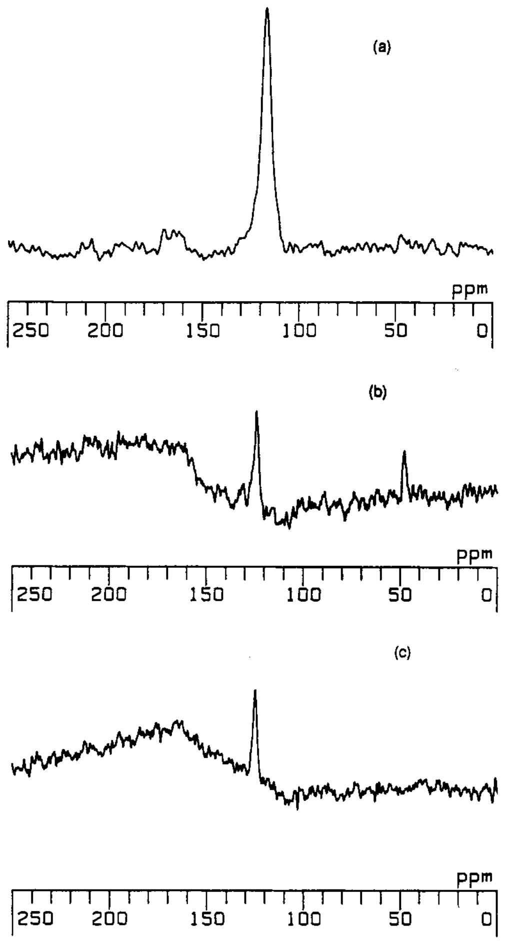

Figure 6. CPID spectra at 300 K after heat treatments of C_2H_4 and O_2 over 2.8% Ag/SiO_2 at (a) 373, (b) 503, and (c) 573 K.

62 and 72 ppm; and peaks at 204, 174, 29, and 18 ppm. Additional small peaks at 198, 159, 134, and 122 ppm are seen in the Bloch decay and CPMAS spectra after heat treatment at 373 K (Figures 8b and 9b).

Discussion

The ^{13}C chemical shifts obtained for the standard compounds dispersed on the catalyst surfaces (Tables 2 and 3) show that there are only small differences between the standard on the Ag catalyst and the standard on the same support without Ag. Except for the formic acid species, which exhibit a range of carboxyl shifts over 9 ppm, the shifts are similar with Al_2O_3 and SiO_2 as the support. These results are consistent with our previous assignments for acetate, formate, and carbonate.[11] The current study has placed the oxalate peak at 168 ppm; therefore, our previous assignment of the 159 ppm peak to oxalate appears incorrect and the origin of this latter peak on the Ag/η-Al_2O_3 catalyst is now uncertain. Table 3 shows the effect of deprotonation on the chemical shifts observed for oxalic, formic, and acetic acids. There is a downfield shift for the deprotonated species, and this is verified in the literature where a chemical shift difference of up to 5 ppm was observed for $RCOO^-$ compared to RCOOH.[18,19] The study of the ^{13}C acetaldehyde standard also shows that the aldehyde species is easily oxidized to acetate on the catalyst surface (Figure 2e). The anhydride standard also reveals a dramatic difference between the shift for the pure compound and that for the adsorbed species. This is attributed to the rapid conversion of acetic anhydride to acetic acid in the presence of hydroxyl groups or adsorbed water; for example, under actual reaction conditions, water is formed due to complete combustion, as verified by the presence of CO_2, and hydroxyl groups are present on the support. These two factors considered together lead us to the conclusion that any anhydride present on the real catalyst would exhibit the acetate-like shifts that have been reported here.

On the basis of the results of these various NMR experiments, we can discuss the epoxidation and combustion reactions of ethylene on the Ag/SiO_2 catalyst in the following manner. The Bloch decay spectra reveal the resonances of all observable ^{13}C nuclei, while the CPMAS spectra show only those ^{13}C nuclei which are close to ^1H nuclei and are not fully mobile. These facts lead us to assign the large resonance in the Bloch decay spectrum at 126 ppm in Figure 4 to gas-phase CO_2. This agrees with the assignment of the 124 ppm peak by Hosseini to gas-phase or weakly adsorbed CO_2 on SiO_2.[12]

Studies of Plischke *et al.*[11] and Hosseini[12] establish beyond doubt the existence of different states of adsorbed ethylene on the catalyst surface. The various forms of ethylene species can be recognized from the line widths and the chemical shifts. Ethylene can resonate between 103 ppm (irreversibly adsorbed on O-covered Ag) and 123 ppm (very high mobility, i.e., weakly adsorbed on the support).[11] Furthermore, rigidly bound ethylene is seen as a broad peak, whereas mobile, weakly bound ethylene yields sharp peaks. The large broad resonance observed between 111 and 120 ppm in Figures 3a and 4a lies between these extremes; therefore, ethylene is weakly adsorbed on the catalyst surface with the downfield shoulder corresponding to C_2H_4 on clean Ag or on SiO_2 and the upfield peak associated with C_2H_4 on an O-covered Ag surface.[11] Figure 1b shows that both species exist. The decrease in intensity of this peak after each incremental heat treatment verifies that the ethylene reacts to form various products. This ethylene peak is clearly seen in the CPMAS experiment (Figure 5), and it survives the dipolar dephasing delay of 50 μs (Figure 6), implying that there is sufficient motion to reduce the dipolar interaction, but that the motion is insufficient to preclude cross-polarization. Table 1 verifies the fact that almost 90% of the ethylene on the surface of this catalyst is reversibly adsorbed, and the CPMAS and CPID results verify that the C_2H_4 species is mobile on the surface. The narrow peak near 123 ppm in Figure 4c appears to correspond to either gas-phase C_2H_4 or, more probably, C_2H_4 weakly adsorbed on the SiO_2 support.[11,12]

The presence of CO_2 in the Bloch decay spectrum prior to any heat treatment of the catalyst, Figure 3a, is a clear indication that the temperature reached during sealing of the glass ampule was sufficient to allow a reaction between C_2H_4 and O_2 in the gas phase or on the hot Pyrex surface in that region of the tube. This occurred even though the lower portion of the ampule, which contained the catalyst, was kept immersed in liquid N_2 during the sealing process. The peak present at 30 ppm in the sample prior to heat treatment probably arises due to β-methyl or β-methylene carbons of alkoxy groups associated with SiO_2.[19] Their mobility is sufficient to make them unobservable with CPMAS. Such species were seen in the same chemical shift region in other studies of Ag/η-Al_2O_3[11] and Ag/SiO_2.[12]

The reduction in the ethylene signal with heat treatment coincides with the emergence of a peak at 47 ppm in the Bloch decay spectrum that we assign to ethylene oxide on oxygen-covered Ag. Hosseini found that ethylene oxide adsorbed on a SiO_2 surface saturated with EO gave a peak at 40 ppm.[12] We found that dilabeled ^{13}C EO on a reduced 2.8% Ag/SiO_2 surface yields a strong resonance at 41 ppm. The resonance at 47 ppm in the oxygen-containing reaction sample is also present in both the CPMAS and CPID spectra at 503 K. The same signal appears as a prominent peak in the Bloch decay spectrum after heat treatment at 448 K, and the two strongest peaks at 47 ppm in the CPMAS spectra occur at 448 and 503 K (Figure 5b,c). This shows that the EO concentration is at a maximum in this temperature range, which is near that used commercially. Heat treatment at 503 K decreases the EO observed in the Bloch decay

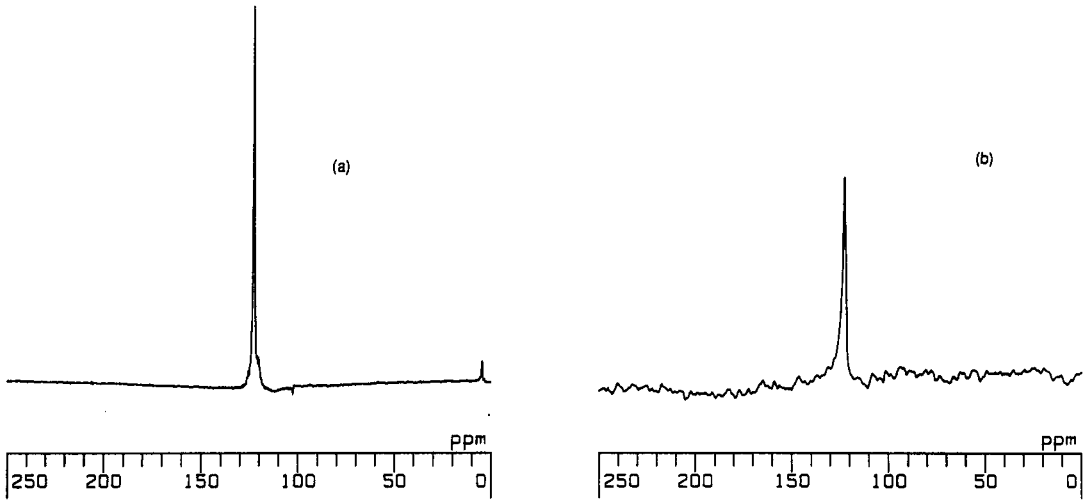

Figure 7. 2.8% Ag/SiO_2 with ethylene adsorbed on an oxygen-covered Ag catalyst after a heat treatment at 623 K (no gas-phase O_2): (a) Bloch decay spectrum and (b) CPMAS spectrum.

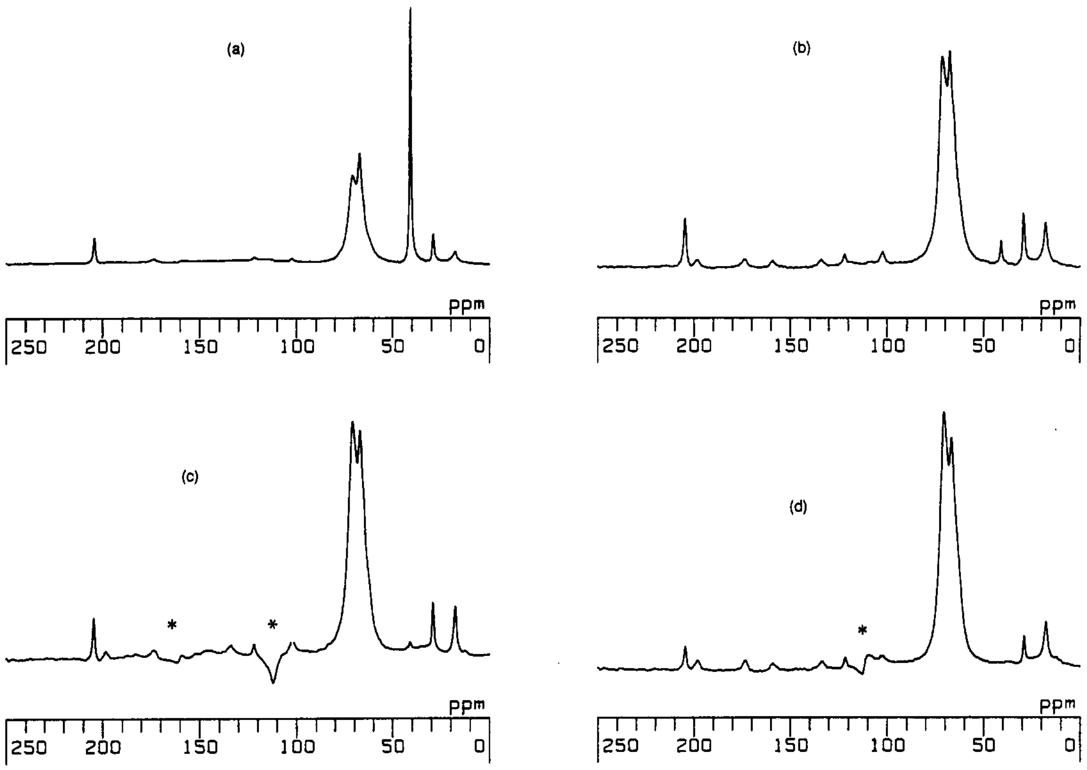

Figure 8. Bloch decay spectra of [$^{13}C_2H_4O$] on reduced 2.8% Ag/SiO_2 at (a) 300 K and after heat treatments at (b) 373, (c) 423, and (d) 473 K. Spinning sidebands are denoted by asterisks.

spectrum as a result of further reaction. At the same temperature, the formation of a new ethylene species at 123 ppm suggests that a reversal of the oxidation process occurs; that is, some of the EO formed decomposes back to very weakly adsorbed or gas-phase ethylene, which is seen in all three types of spectra at 503 K. This is a well-documented reaction for ethylene oxide,[1,12,21] and it may be facilitated here if excess ethylene exists and the oxygen is consumed first.

Previous studies have indicated that, once formed, EO on the surface can isomerize to acetaldehyde, especially on acidic sites on oxide surfaces;[1] however, no peaks were observed in the carbonyl or methyl chemical shift region expected for acetaldehyde. Madix and co-workers have shown on a Ag(110) single crystal that acetaldehyde can be oxidized to acetate, which in turn decomposes to formate and then can convert to CO_2 at temperatures above 400 K.[22,23] All of these groups except the aldehyde were indeed observed on a Ag/η-Al_2O_3 catalyst which showed very poor selectivity to EO and primarily gave complete combustion;[11] however, no peaks corresponding to acetate or aldehyde were observed on this Ag/SiO_2 catalyst, which has a much higher selectivity to EO.[14] Van Santen and Kuipers have concluded that isomerization of EO is suppressed on O-covered Ag and favored on an alumina support.[1] The barely discernible peak seen at 64 ppm in the Bloch decay spectrum in Figure 4d is attributed to the formation of SiO—CH_2CH_2OH on the SiO_2 surface. Such species have also been reported on Al_2O_3 and SiO_2 surfaces by Plischke *et al.*[11] and Hosseini.[12]

These is a carbonyl resonance clearly visible near 164 ppm in all the CPMAS spectra, even in that obtained before heat treatment. This peak was also seen by Plischke *et al.* on Ag/η-Al_2O_3[11] and must be either formate or a protonated species related to oxalate because it can be observed with cross-polarization. This species is easily seen in the CPMAS spectra, and its intensity is much reduced in the corresponding CPID

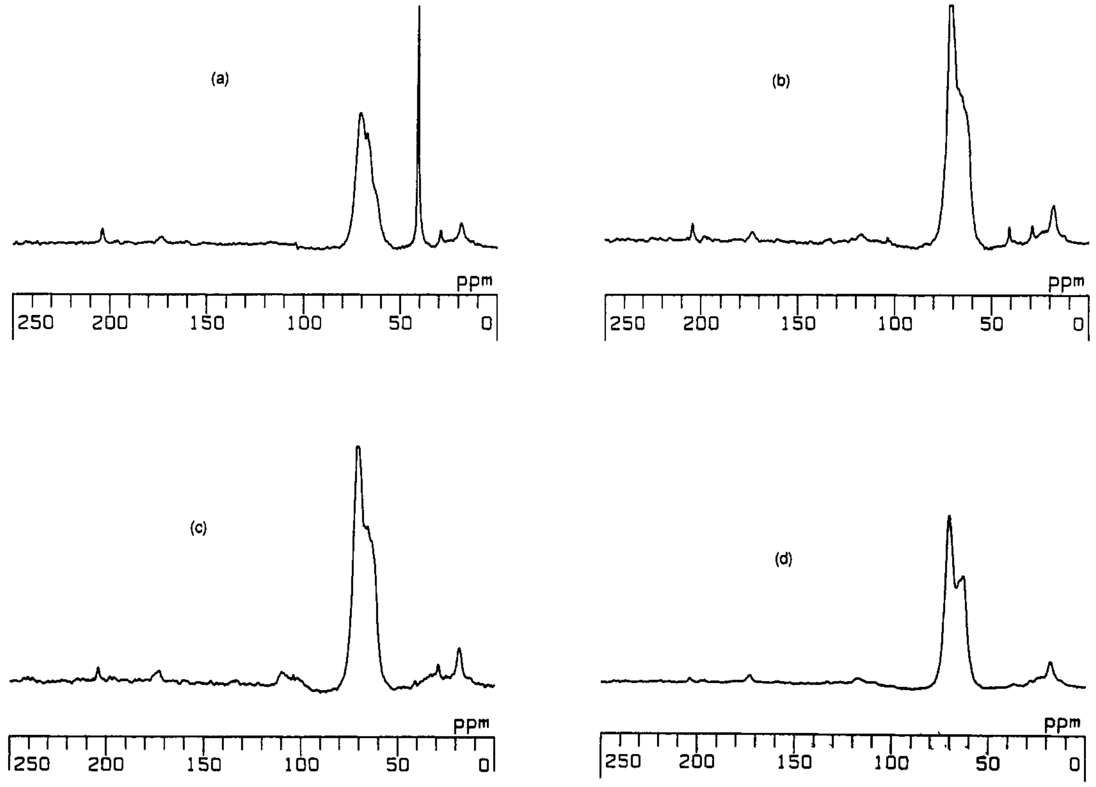

Figure 9. CPMAS spectra of [$^{13}C_2H_4O$] on reduced 2.8% Ag/SiO_2 at (a) 300 K and after heat treatments at (b) 373, (c) 423, and (d) 473 K.

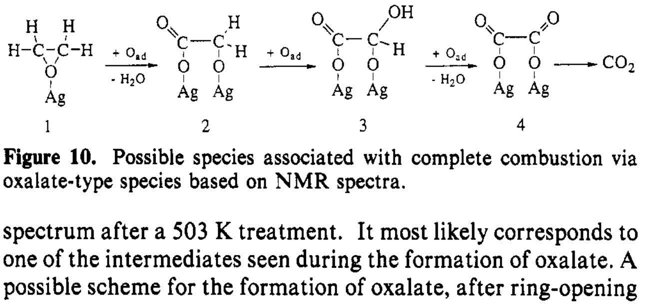

Figure 10. Possible species associated with complete combustion via oxalate-type species based on NMR spectra.

spectrum after a 503 K treatment. It most likely corresponds to one of the intermediates seen during the formation of oxalate. A possible scheme for the formation of oxalate, after ring-opening of the EO and its subsequent adsorption on the surface, is outlined in Figure 10. The glycolate species represented by intermediate 2 in Figure 10 has been proposed previously by Sault and Madix.[23] After its formation the oxalate then undergoes complete combustion to CO_2. Oxalate-type species were reported by Force and Bell in their IR spectroscopic study of EO formation on SiO_2-supported Ag.[6,7]

Figure 7 shows the Bloch and CPMAS spectra for 2.8% Ag/SiO_2 with excess ethylene in the presence of only irreversibly adsorbed oxygen. The appearance of a single sharp peak at 122 ppm common to both the single-pulse and CPMAS spectra verifies that most of the ethylene remains largely unreacted, as expected, and it represents ethylene weakly adsorbed on the SiO_2 surface.[12] The smaller peak at 120 ppm could represent ethylene on the Ag surface.[11] No peak for CO_2 or EO was observed due to the small amount of oxygen (and hence products) present, and no carbonyl resonances were apparent. This is consistent with the work of Van Santen and De Groot in which no EO production was observed unless an overpressure of O_2 was present.[9] They observed an increase in EO formation with increasing O_2 gas-phase pressure because of the rapid exchange between subsurface and surface oxygen. The small peak around 5 ppm in the Bloch decay spectrum (Figure 7a) was also observed by Hosseini *et al.* and is probably due to ethane,[12] although its origin is not clear.

The spectra in Figures 8 and 9 for the ^{13}C ethylene oxide on reduced 2.8% Ag/SiO_2 in the absence of adsorbed oxygen can be interpreted as follows: The sharp peak at 41 ppm seen in the spectra at 373 K and at room temperature corresponds to EO. This peak begins to disappear after the heat treatment at 423 K. The assignment to EO agrees with the literature value of 41 ppm[19] and the assignment at 40 ppm made by Hosseini.[12] The broad peaks between 62 and 72 ppm, seen in all the spectra in Figures 8 and 9, are attributed to polymer and glycol products formed on the catalyst surface. These results indicate that EO easily converts to polymers (polyethylene oxides) or glycol on reduced Ag/SiO_2.

Some of the ^{13}C-dilabeled EO standard isomerized to acetaldehyde, as can be inferred from the peaks seen at 204 and 29 ppm, which are attributed to the carbonyl and methyl resonances, respectively, of acetaldehyde.[19] This is also in good agreement with the carbonyl shift information obtained for the acetaldehyde standard. Also seen in all the spectra are peaks at 174 and 18 ppm, which we assign to acetic acid formed by oxidation of acetaldehyde on the catalyst surface. In addition, peaks at 122 and 102 ppm are observed, which can be assigned to weakly bound C_2H_4 on SiO_2 and strongly bound C_2H_4 on O-covered Ag. This clearly implies decomposition of EO to C_2H_4 and oxygen adsorbed on Ag, thus providing the capability of further oxidation of acetaldehyde to acetic acid. This oxidation is readily catalyzed by ionic Ag, and Hosseini also saw acetic acid and ethylene in addition to EO after heating a Ag/SiO_2 catalyst to 523 K.[12] They also assigned peaks at 64 and 71 ppm to $\equiv SiOCH_2CH_2OH$ and $\equiv Si(OCH_2O)_nCH_2OH$ formed as a result of interaction with hydroxyl groups on the SiO_2 support. These structures are similar to the PEO polymers and/or glycol indicated by our experiments; however, Hosseini did not find any evidence for isomerization of EO to acetaldehyde catalyzed by Ag.[12] The peaks seen at 134 and 159 ppm are due to the hydroquinone stabilizer in the EO. The peak at 198 ppm is assigned to formaldehyde.[19]

The small peaks seen in the 100–103 ppm range correspond to ethylene formation as a result of decomposition of EO. This ethylene is strongly bound to the surface, but the presence of a certain amount of weakly adsorbed ethylene is indicated by the resonance seen at 122 ppm.[11]

Summary

The measurement of the chemical shifts of soluble standard compounds containing formate, anhydride, carbonate, and oxalate groups which were impregnated onto Ag/SiO_2 and Ag/Al_2O_3 catalysts has verified most of the assignments made earlier.[11,12] Such calibration is necessary because the chemical shifts observed not only can differ noticeably from those measured with the pure compound but also vary with the support used and the concentration on the oxide surfaces. The tabulation of these shifts in this study allows identification of intermediates formed in the interaction between oxygen and ethylene over silver surfaces. The results of this investigation with standard compounds on the catalyst and support surface provide chemical shift assignments for the following compounds: ethylene oxide, formic acid, formate, oxalic acid, oxalate, acetic anhydride, acetaldehyde, and carbonate. The shifts determined were representative of the species in the adsorbed state on oxide surfaces and hence sometimes differed from the values obtained for the pure compounds.

The incremental heat treatment studies of ^{13}C-labeled ethylene oxide on reduced Ag/SiO_2 revealed a variety of decomposition products, most of which could be identified. Acetic acid was clearly observed; the presence of acetaldehyde and formaldehyde was determined; structures resembling polymers of ethylene oxide or glycols were seen as broad peaks; and both strongly and weakly adsorbed ethylene was detected.

With an unpromoted $Ag/\eta\text{-}Al_2O_3$ catalyst studied previously which gave primarily complete combustion products and very low selectivities to EO of about 10%, even with ethylene dichloride in the feed stream,[14] acetate, formate, carbonate, and oxalate groups were identified using CPMAS NMR.[11] The first three surface species have been directly associated with the complete combustion of ethylene on Ag,[1,20,22,23] which is consistent with the catalytic behavior observed with Ag dispersed on this high surface area $\eta\text{-}Al_2O_3$. No EO was detected by NMR.

In contrast, Ag dispersed on SiO_2 gave selectivities to EO of over 60% with ethylene dichloride in the feed and, even in the absence of this promoter, selectivities of 55% could be obtained.[14] On the basis of our studies with a Ag/SiO_2 catalyst after reaction between $^{13}C_2H_4$ and oxygen, the presence of CO_2, gas-phase and adsorbed species of ethylene, ethylene oxide, and formate or protonated oxalate species was shown. Small amounts of alkoxide species on the SiO_2 were also observed. The absence of any aldehyde or acetate species on this catalyst is consistent with its higher selectivity to EO, and it implies a lower isomerization activity when Ag is dispersed on a more inert support like SiO_2. The absence of acetate species and the presence of oxalate-type species allows the possibility that another route may exist for complete oxidation that does not require an isomerization step, i.e., by the stepwise removal of hydrogen atoms from adsorbed ethylene to form a surface oxalate species, perhaps including a monoprotonated intermediate, which then decomposes to produce CO_2. Additional NMR studies with promoted Ag catalysts will be required to confirm this possible parallel reaction route to CO_2.

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