

CO adsorption on supported and promoted Ag epoxidation catalysts

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Abstract

CO was used to probe the nature of adsorption sites on Ag/ α -Al₂O₃ epoxidation catalysts and to investigate the effect of Cs and Cl promoters by employing diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and chemisorption measurements. In contrast to previous studies, IR absorption bands for CO chemisorbed on reduced, supported Ag crystallites were observed; however, CO adsorption occurred on only 3–7% of the total Ag surface at 300 K and coverage depended on both the pretreatment and CO pressure utilized. No irreversible CO adsorption occurred on the alumina, whereas linearly bonded CO was the dominant species on the metallic Ag sites. After a 30-min purge, the bands due to these chemisorbed forms of CO decreased in intensity while a band due to bridge-bonded CO increased in intensity, which implies that CO reoriented as the surface concentration of CO decreased. In the presence of Cs, similar behavior was observed and the band intensity of the bridge-bonded CO increased. After reduction at 673 K, cesium suboxides appeared to be formed based on the formation of carbonyl complexes at 2028, 1950, and 1869 cm⁻¹. On reduced Ag catalysts, electronic effects of Cs and Cl were observed and adsorbed CO gave a lower frequency, i.e., 2018 and 2009 cm⁻¹ for Cs-promoted samples reduced at 473 and 673 K, respectively, due to an increase in the electron density on surface Ag atoms, while this band occurred at a higher frequency of 2129 cm⁻¹ with a CsCl-promoted Ag catalyst due to a net decrease in the electron density on surface Ag atoms. After CO adsorption on O-covered Cs-promoted and CsCl-promoted catalysts, a band between 1520 and 1491 cm⁻¹ existed which was assigned to a COO⁻ stretching mode in a carbonate species formed on composite AgCs_xO_y sites. These studies with CO provide evidence that reduction at 673 K following a calcination step can lead to redistribution of Cs atoms.

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1. Introduction

Direct olefin epoxidation by molecular oxygen is an extremely important class of catalytic reactions and silver is a unique catalyst for the selective oxidation of ethylene and other olefins containing nonallylic hydrogen as well as kinetically hindered olefins. The epoxidation of butadiene over silver catalysts is a new industrial process which is a successful example of higher olefin epoxidation, and the product of this reaction, 3,4-epoxy-1-butene (EpB), is an important organic intermediate from which a variety of C₄-oxygenated compounds can be produced [1–5]. There are many similarities between the ethylene and butadiene epoxidation processes; for example, the catalyst is composed of Ag dispersed on low surface area α -Al₂O₃ and promoted with Cs and Cl, with the latter provided continuously

in the form of chlorobutane or ethylene dichloride in the feed at ppm levels. However, the optimum catalyst composition is different, thus it is important to better understand the compositional and structural features of the novel Ag catalyst for EpB so that its selectivity, activity, and lifetime can be improved.

CO has been extensively used as a probe molecule on most of the transition metals, but there have been relatively few studies of carbon monoxide adsorption on silver. Spectral characteristics of CO depend strongly on the electronic state of the adsorption site, and the charge on the metal carbonyl (i.e., the oxidation state of the metal) has a large effect on the vibrational frequencies of these carbonyl complexes [6]. Moreover, because adsorbed CO exhibits a high extinction coefficient in the infrared, it is a useful chemisorption probe of adsorbate-site geometry using IR techniques. Thus it can provide information about the influence of pretreatment on the nature of adsorption sites on dispersed silver epoxidation catalysts, the effect of

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promoters, and the adsorption of ethylene and butadiene because CO is also a weak base like these alkenes.

Previous work with reflection–absorption infrared spectroscopy (RAIRS) reported that no CO adsorption was observed at 77 K [7], but below 35 K, a band at 2137 cm^{-1} due to physisorbed CO on Ag (111) was observed by employing high-resolution electron energy loss spectroscopy (HREELS) [8]. Although the temperature was low enough, no significant CO adsorption was observed on this silver crystal surface, and it was concluded that the adsorption of CO on clean silver is substantially weaker than that on Cu or transition metals. On silver films, vibrational bands for CO have been seen in the 2160 to 1930 cm^{-1} spectral region at temperatures ranging from 2 to 300 K by utilizing different vibrational spectroscopy techniques [9–16]. The various bands observed over this wide temperature region may be explained by the different temperatures and pressures utilized, the crystal planes exposed, the cleanliness of the surface, and the vibrational techniques used. However, the silver–CO interaction was weak in all these studies, as reported for single crystals.

CO adsorption on supported silver catalysts had not produced any detectable band due to a metallic silver–CO interaction [17–19], and it was concluded that CO did not adsorb on metallic Ag particles, although the effect of pretreatment, pressure, and surface cleanliness had not been investigated thoroughly. In contrast, a band between 2200 and 2150 cm^{-1} was observed with some calcined supported Ag catalysts and assigned to a $\text{Ag}^+\text{--CO}$ complex [17–22]. The different frequencies were attributed to the different supports that had been used. Similarly to the studies of Ag single crystals and films, the adsorbed CO species were found to be moderately unstable and, in most of the cases after evacuation at ambient temperature, the $\nu(\text{CO})$ band disappeared or decreased in intensity.

The present study was conducted to examine CO adsorption on dispersed silver epoxidation catalysts in detail to gain insight into the nature of adsorption sites on both unpromoted and promoted catalysts. The effects of different pretreatments and two promoters, namely cesium and chloride, were studied, and the behavior of CO adsorption on $\alpha\text{-Al}_2\text{O}_3$, unsupported Ag powder, unpromoted

$\text{Ag}/\alpha\text{-Al}_2\text{O}_3$, $\text{Cs}/\alpha\text{-Al}_2\text{O}_3$, Cs-promoted $\text{Ag}/\alpha\text{-Al}_2\text{O}_3$, and CsCl-promoted $\text{Ag}/\alpha\text{-Al}_2\text{O}_3$ catalysts was investigated at ambient temperatures using DRIFTS (diffuse reflectance infrared Fourier transform spectroscopy) to monitor surface CO species.

2. Experimental

Ag catalysts, prepared by a wet impregnation technique, were obtained from the Eastman Chemical Company in Kingsport, TN. Silver oxalate was the precursor and a solution of ethylenediamine, water, and silver oxalate was prepared. For the promoted catalysts, either CsCl or CsNO_3 was also added to the solution. The $\alpha\text{-Al}_2\text{O}_3$ support (Norton Corp., SA 5562, $0.78\text{ m}^2/\text{g}$) was added to the stirred solution, and the system was dried at 335 K to remove excess water. Afterwards, the sample was calcined in air at 598 K for 30 min.

The unpromoted catalyst used for this study is designated UNP-II. Two nominal 1000 ppm Cs-promoted Ag catalysts and one nominal 1000 ppm $\text{Cs}/\alpha\text{-Al}_2\text{O}_3$ sample, designated CsN (1174), CsCl (994), and CsN (1000, no Ag), respectively, were prepared. The prefixes CsN and CsCl indicate either CsNO_3 or CsCl as the precursor Cs compound, and the number in parentheses indicates the analyzed Cs content in ppm. In addition to these catalysts, experiments were performed with silver powder (Alfa Aesar, 99.9995%) and pure $\alpha\text{-Al}_2\text{O}_3$.

The catalysts were subjected to either a low-temperature (LT) or a high-temperature (HT) pretreatment prior to CO adsorption, and the surface was left in either a reduced (I) or an O-covered (II) state. The pretreatment procedures are given in Table 1, with the temperature used in the HT pretreatment shown in parentheses.

Two different techniques were used to characterize these silver catalysts. In situ DRIFTS was employed using a Mattson Research Series 10000 spectrometer coupled with a Harrick Scientific DRA diffuse reflection cell with NaCl windows. A gas handling system and temperature controller were combined with this infrared system to allow in situ sample pretreatment, details have been provided else-

Table 1
Catalyst pretreatment procedures

I-LT (HT)-Reduced
1. Heat from 300 K to 523 (773) K and calcine for 2 h at 523 (773) K in 20% O_2 at a total flow of 50 sccm;
2. Reduce for 1 h at 473 (673) K in 20% H_2 at a total flow of 50 sccm;
3. Purge at 473 (673) K for 30 min under He flow or evacuate at 473 (673) K for 30 min;
4. Cool to ambient temperature;
5. Introduce 10% CO in He for all catalysts or 10 to 80% CO in He for only UNP-II for 30 min at a total flow of 20 sccm.
II-LT (HT)-O-covered
1. After applying Method I-LT (HT), introduce 10% O_2 in He for 30 min at 443 K at 20 sccm total flow;
2. Purge at 443 K for 30 min under flowing He, or evacuate at 443 K for 30 min;
3. Cool to ambient temperature, and introduce 10% CO in He (20 sccm total flow).

where [23,24]. Ultra-high-purity (UHP) grade He and H₂ (99.999%, MG Ind.) were further purified by flowing them through indicating Oxytraps (Alltech Assoc.), while every gas, including O₂ (99.999%, MG Ind.), was flowed through its own molecular sieve trap. CO (99.99%, Matheson) was used after it was passed through a Drierite trap and a 5A molecular sieve trap (Alltech Assoc.) to remove water and CO₂, respectively. Precise gas flow rates were maintained using mass flow controllers (Tylan Corp., Model FC-260). The gases were fed at atmospheric pressure in all pretreatments and experiments.

Interferograms were based on 1000 scans (5.35 min) at a resolution of 4 cm⁻¹, a gain of 4, and an iris setting of 50, and data acquisition and processing were performed with commercial Winfirst software. The interferogram for each sample and its corresponding background interferogram were then Fourier transformed to its equivalent frequency component spectrum. After the sample was loaded into the DRIFTS cell, the catalyst was purged overnight under a He flow and then subjected to one of the four pretreatments in situ and cooled to 300 K, at which time the first interferogram (minute 0) was taken. Following this, the catalyst was exposed to a mixture of 10% CO and 90% He at 300 K for 30 min; for the UNP-II catalyst only, the partial pressure of CO was also varied between 10 kPa (10% CO) and 80 kPa (80% CO). After 30 min of exposure to CO, the second interferogram was collected (minute 30), but for some samples, additional interferograms were also recorded during the 30-min exposure to CO. The sample was then purged with He for 30 min and another interferogram was collected (minute 60) at 300 K to provide a third spectrum. The first interferogram was used as the background for both the second and third interferograms. The results are presented as Absorbance because the Absorbance and Kubelka–Munk spectra were typically similar, but the K–M function does not display negative bands.

Chemisorption measurements were performed on the UNP-II catalyst in a stainless steel gas adsorption system capable of a vacuum of 10⁻⁷ Torr. The system was equipped with a Balzers Type TPU 170 turbomolecular pump (Pfeiffer Vacuum Technol.) backed by an Edwards Model RV5 mechanical pump to obtain a high dynamic vacuum, which was monitored by a Granville–Phillips Model 260 gauge controller. Changes in gas pressure during the volumetric adsorption measurements of CO and O₂ were detected using a differential pressure gauge (MKS Instr., Type 270B) connected to a Baratron Type 310CA pressure sensor, while the temperature was monitored by an Omega Model 412B-J digicator. Details of this adsorption system have been given elsewhere [25]. O₂ uptake on UNP-II at 443 K was measured after applying either the I-LT or the I-HT pretreatments, while CO uptake was measured on both clean and O-covered UNP-II surfaces at ambient temperature. About 4 g of UNP-II catalyst was used for the experiments.

Table 2
Composition of Ag catalysts

Catalyst	Silver ^a (%)	Cesium ^b (ppm)	Chlorine ^c (ppm)	<i>d</i> ^d (nm)
UNP-II	14.9	0	0	275
CsN (1174)	10.8	1174	0	354
CsN (1000, no Ag)	0	1000	0	–
CsCl (994)	13.1	994	310 ^e	–

^a Analyzed by ICP-OES.

^b Analyzed by AAS.

^c Analyzed by XRF.

^d Particle size calculated based on SEM analysis.

^e Nominal content based on cesium content.

3. Results

Silver loadings (wt%) in these Ag/ α -Al₂O₃ catalysts were determined at Eastman Chemical Company by inductively coupled plasma optical emission spectroscopy, while Cs and Cl contents (in ppm) were measured by atomic absorption spectroscopy and X-ray fluorescence, respectively. The results of these analyses and the average Ag particle sizes are listed in Table 2.

3.1. α -Al₂O₃ support

DRIFT spectra of CO adsorbed on alumina, on unsupported and supported silver, and on the promoted supported silver catalysts at 300 K were obtained after a chosen pretreatment. Figure 1 displays the spectra of CO adsorbed at 300 K on α -alumina subjected to a I-LT pretreatment. The initial spectrum under 10 kPa CO exhibited peaks near 2213 and 2138 cm⁻¹, which were assigned to CO adsorbed on coordinatively unsaturated tetrahedral Al³⁺ ions and weakly chemisorbed CO, respectively, on the alumina surface [6,26]. Purging the cell in He for 30 min resulted in the disappearance of the 2213 and 2138 cm⁻¹ bands, indicating that all CO adsorption on the alumina was reversible. Bands near 1710, 1642, and 1060 cm⁻¹ were also observed, with the latter two assigned to the O–H bend-

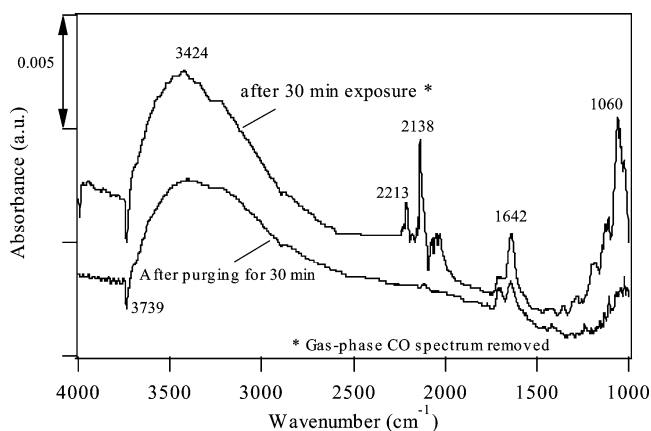


Fig. 1. DRIFT spectra of adsorbed CO on α -Al₂O₃ at 300 K after I-LT pretreatment; $P_{CO} = 10$ kPa.

Table 3
Chemical analysis of α -Al₂O₃ support

Compound	α -Al ₂ O ₃	SiO ₂	Na ₂ O	K ₂ O	CaO	MgO	TiO ₂	Fe ₂ O ₃
Content (wt%)	99.7	0.1	<0.01	0.003	0.088	<0.01	0.002	0.038

ing mode of chemisorbed water and an Al–O stretching mode, respectively [6], while the band at 1710 cm⁻¹ may be due to carbonyl complexes caused by impurities in the alumina. A chemical analysis for impurities in the alumina was conducted and the results are given in Table 3. Similar IR features were observed after a I-HT pretreatment [27] and thus are not shown here.

3.2. Ag powder

Because there are no significant IR features associated with CO adsorbed on alumina, any peaks obtained with the Ag/ α -Al₂O₃ catalysts can be directly related to species adsorbed on Ag. To further verify this, spectra of CO adsorbed on Ag powder at 300 K after pretreatment I-LT were acquired (Fig. 2). The spectrum obtained under 10 kPa CO showed a band centered around 2045 cm⁻¹, which can be assigned to CO linearly bonded to a single Ag atom, and another band at 2140 cm⁻¹, which is assigned to CO interacting with a Ag cation and indicates that some surface oxygen still remained after the I-LT pretreatment. A 30-min purge in He resulted in the disappearance of the bands at 2140, 2056, and 2046 cm⁻¹, and a band at 2030 cm⁻¹ remained with decreased intensity, showing that much of the linearly bonded CO was weakly chemisorbed on the surface. On the other hand, a band at 1952 cm⁻¹ increased in intensity, and this can be assigned to bridge-bonded CO at this lower coverage on metallic silver [28,29]. This Ag powder sinters significantly after a high-temperature reduction, so CO adsorption on that surface was not studied.

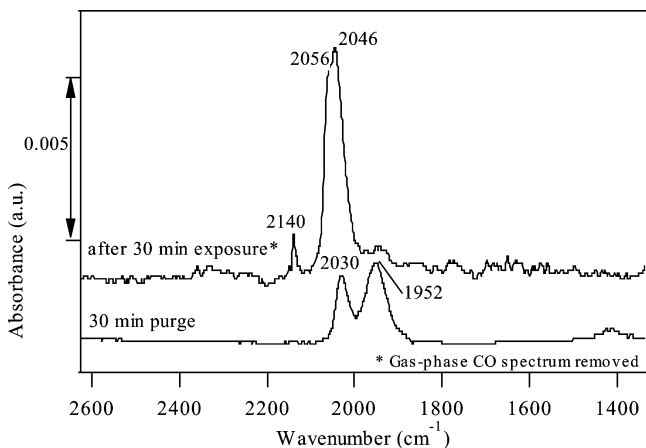


Fig. 2. DRIFT spectra of CO adsorbed at 300 K on Ag powder after a I-LT pretreatment; $P_{\text{CO}} = 10$ kPa.

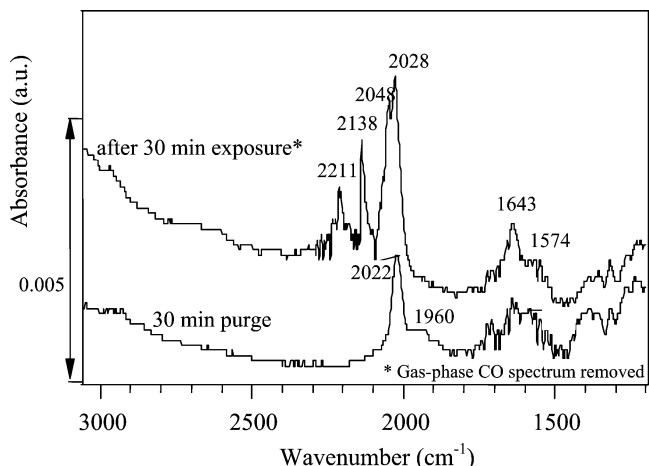


Fig. 3. DRIFT spectra of CO adsorbed on UNP-II at 300 K after a I-LT pretreatment; $P_{\text{CO}} = 10$ kPa for the first spectrum.

3.3. Ag/ α -Al₂O₃

Figure 3 shows DRIFT spectra of CO adsorbed at 300 K on a fresh sample of UNP-II after calcination at 523 K and reduction at 473 K (I-LT pretreatment). The weakly adsorbed CO at 2211 cm⁻¹ is due to CO adsorption on alumina and the band at 2138 cm⁻¹ may have contributions from CO on both alumina and partially reduced silver sites, while the peaks at 2048 and 2028 cm⁻¹ are assigned to linearly adsorbed CO on metallic silver sites, such as those observed with Ag powder. The OH stretching region exhibited a broad band similar to that obtained after CO adsorption on alumina; therefore, only the region 3000–1200 cm⁻¹, which again shows a weak bending mode of chemisorbed water, is displayed. After purging, linearly bonded CO remained at 2022 cm⁻¹ along with a shoulder at 1960 cm⁻¹ due to bridge-bonded CO.

After a I-HT pretreatment, CO adsorption on UNP-II at 300 K gave a narrower, stronger peak with a maximum at 2055 cm⁻¹ and a shoulder at 2040 cm⁻¹ along with a weak

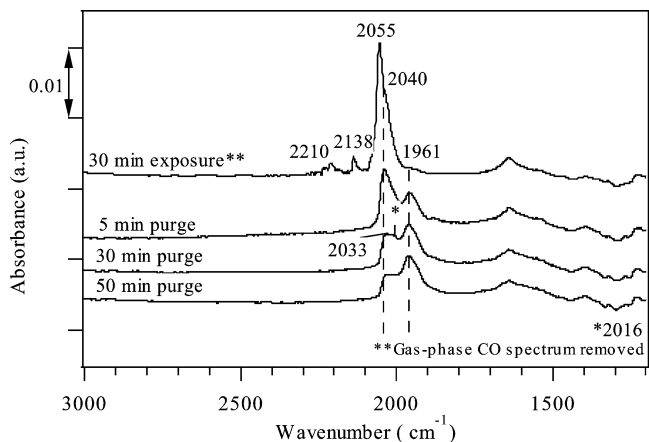


Fig. 4. DRIFT spectra of CO adsorbed on UNP-II at 300 K after a I-HT pretreatment; $P_{\text{CO}} = 10$ kPa.

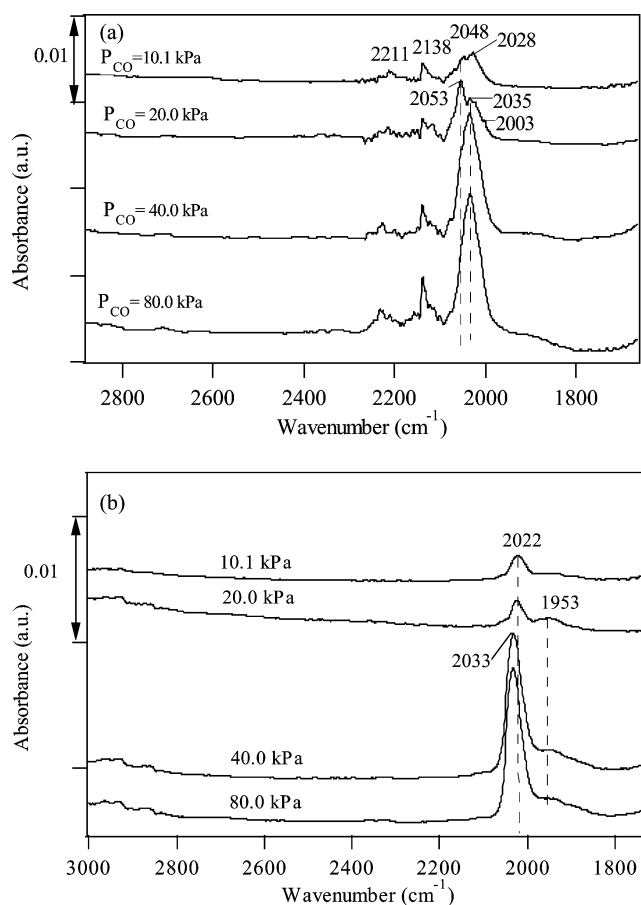


Fig. 5. DRIFT spectra of CO adsorbed on UNP-II at 300 K after a I-LT pretreatment: (a) after 30-min exposure to CO at each pressure (gas-phase CO spectrum removed); (b) irreversibly adsorbed CO after a 30-min purge following each exposure.

1961 cm^{-1} band, and the band intensities are appreciably higher than those observed after a I-LT pretreatment (Fig. 4). Purging resulted in a reduction of peak intensity for the linearly bonded CO, with a 2033 cm^{-1} band remaining, while the intensity of bridge-bonded CO at 1961 cm^{-1} increased. The intensity of the band did not change after an additional 20 min of purging. The observed bands were similar to those obtained with the silver powder after a I-LT pretreatment, implying that this supported silver catalyst (UNP-II) cannot be reduced and/or cleaned as easily as the unsupported UHP Ag powder.

Figures 3 and 4 illustrate CO adsorption on the unpromoted catalyst at a pressure of 10 kPa after either a I-LT or a I-HT pretreatment, and Figs. 5 and 6 display the pressure-dependent changes in CO adsorption on this Ag catalyst. After CO adsorption at each pressure (Figs. 5a and 6a), the system was purged for 30 min and a spectrum was taken, as shown in Figs. 5b and 6b after each pretreatment. Before CO was introduced at different pressures, the corresponding pretreatment was given to the catalyst each time. For the catalyst given the I-LT pretreatment, an increase in CO pressure from 10 to 40 kPa resulted in a dramatic increase in the peak intensity in the spectral region near 2000 cm^{-1} . The

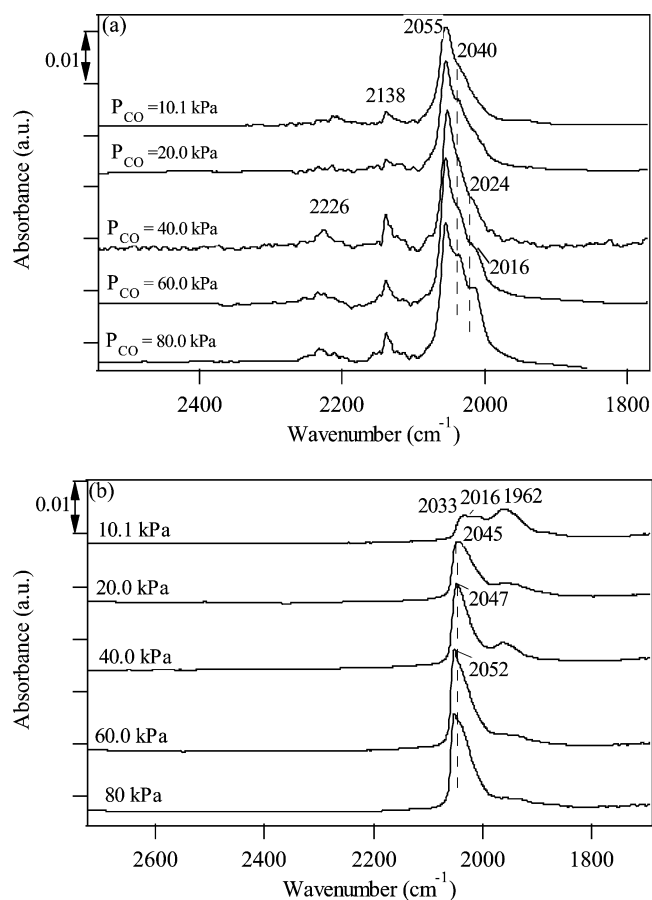


Fig. 6. DRIFT spectra of CO adsorbed on UNP-II at 300 K after a I-HT pretreatment: (a) after 30-min exposure to CO (gas-phase CO spectrum removed); (b) irreversibly adsorbed CO after a 30-min purge following to each exposure.

band at 2028 cm^{-1} was blue-shifted to 2035 cm^{-1} as the CO pressure increased from 10 to 20 kPa, which indicates a dipole–dipole interaction between the adsorbed molecules, and the peak position did not shift further as the pressure increased to 80 kPa. Similarly, a weak band at 2048 cm^{-1} shifted to 2053 cm^{-1} as pressure increased. After purging, a predominant band at either 2022 or 2033 cm^{-1} , depending on the previous CO pressure, was observed along with a weaker band at 1953 cm^{-1} , and the band near 2050 cm^{-1} disappeared (Fig. 5b).

After calcination at 773 K and reduction at 673 K (I-HT pretreatment), the pressure dependency shown in Fig. 6 was similar to that observed on the LT-treated catalyst, although the peak intensities were substantially higher, and a shoulder at 2016 cm^{-1} was also observed at pressures above 20 kPa. When the CO pressure was increased to 80 kPa, distinct bands near 2040 and 2016 cm^{-1} were observed but the 2055 cm^{-1} peak still predominated. Similarly to the LT-treated catalyst, the 1962 cm^{-1} band did not develop until the cell was purged with He. After a purge of the sample exposed to 10 kPa CO, most of the linear-bonded CO was removed and a weak band remained between 2010 and 2035 cm^{-1} , while the main band was now at 1962 cm^{-1} .

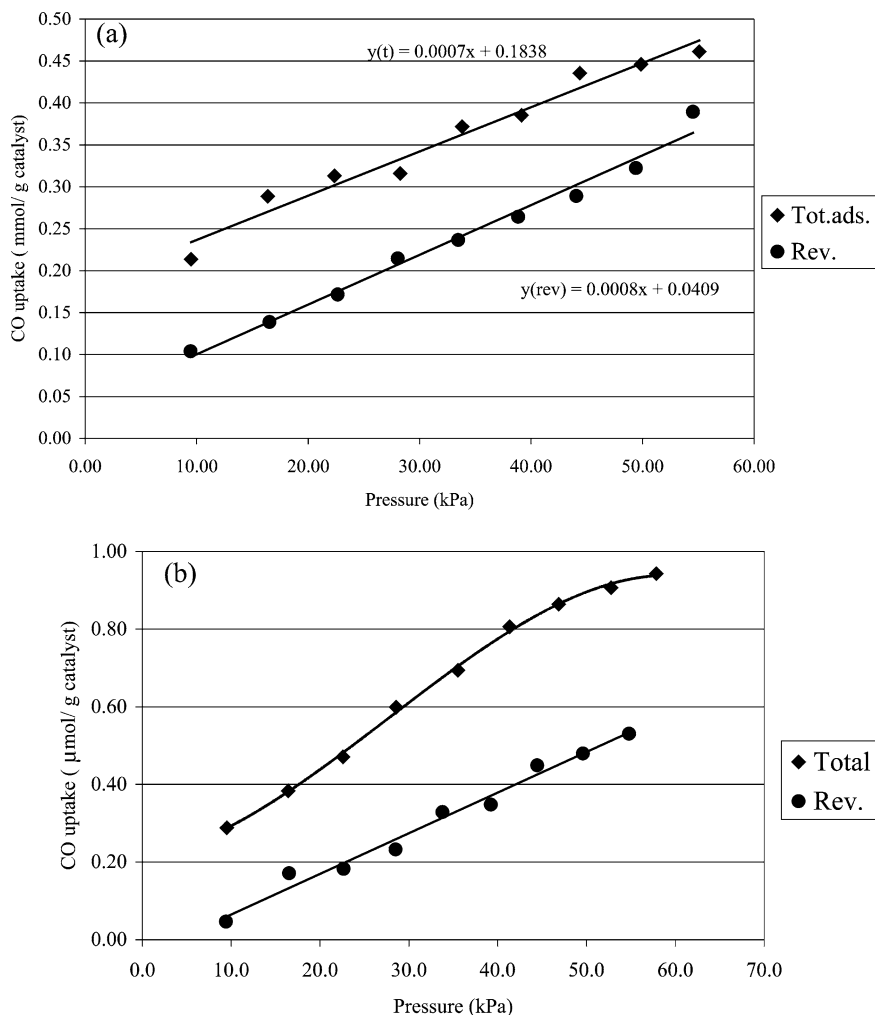


Fig. 7. CO isotherms at 300 K on UNP-II (a) after I-LT pretreatment; (b) after I-HT pretreatment.

As the pressure increased, a predominant band appeared between 2045 and 2052 cm^{-1} .

In addition to the DRIFTS studies, CO uptakes on a clean UNP-II catalyst at 300 K were determined after either a I-LT or a I-HT pretreatment, and Figs. 7a and 7b display the adsorption isotherms for this catalyst. After reduction at 473 K (I-LT), the average irreversible uptake was 0.15 $\mu\text{mol CO/g catalyst}$. After reduction at 673 K, the initial CO uptake did not depend linearly on the CO pressure; hence, at low pressures below 13 kPa the irreversible CO uptake was about 0.2 $\mu\text{mol/g catalyst}$, and the irreversible uptake at pressures above 40 kPa was 0.4 $\mu\text{mol CO/g catalyst}$. The “O” uptakes at 443 K, which give the total number of surface silver atoms, Ag_s , i.e., $2\text{Ag}_s + \text{O}_2 \rightarrow 2\text{Ag}_s\text{O}$, were 4.6 or 5.6 $\mu\text{mol O/g catalyst}$ after reduction at 473 or 673 K, respectively. These values show that full monolayer coverages of CO on Ag are not achieved, as discussed later.

3.4. $\text{Cs}/\alpha\text{-Al}_2\text{O}_3$

To examine the effect of cesium on Ag, CO was first adsorbed on the $\text{Cs}/\alpha\text{-Al}_2\text{O}_3$ sample, CsN (1000, no Ag).

Figure 8 displays spectra for $\text{Cs}/\alpha\text{-Al}_2\text{O}_3$ after exposure to CO at 300 K following either a I-LT or a I-HT pretreatment. The initial spectrum, obtained under 10 kPa CO following a I-LT pretreatment, exhibited weak bands which corresponded to CO adsorption on the alumina and no bands were discernible due to CO adsorption on Cs, as indicated by the spectrum following a purge; however, a LT pretreatment is not expected to significantly reduce any Cs oxide phase [30]. After reduction at 673 K, however, strong bands developed at 2028, 1950, and 1869 cm^{-1} , as demonstrated in Fig. 8. The intensities of all bands decreased after a purge, but the relative intensity of the band at 2028 cm^{-1} increased, thus implying that the adsorbed species giving bands at 1950 and 1869 cm^{-1} can be removed more easily from the surface. Besides these three bands, additional ones occurred at 1660, 1593, and 1360 cm^{-1} , which can be attributed to carbonate compounds [31].

3.5. $\text{Cs-Ag}/\alpha\text{-Al}_2\text{O}_3$

CO adsorption on CsN (1175) at 300 K was conducted under 10 kPa CO after a I-LT pretreatment, and CO bands

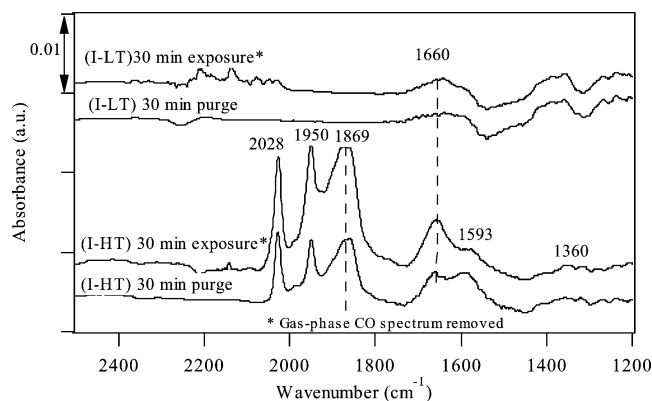


Fig. 8. DRIFT spectra of CO adsorbed on CsN (1000, no silver) after either a I-LT pretreatment or a I-HT pretreatment; $P_{\text{CO}} = 10$ kPa.

at 2052, 2028, 1953 cm^{-1} due to CO adsorption on the silver and 1652, 1507, and 1347 cm^{-1} due to carbonate species were observed, as shown in Fig. 9a. Bands at 1652 and 1347 cm^{-1} were also observed on Cs/ α - Al_2O_3 and assigned to cesium carbonate species; however, no band at 1507 cm^{-1} was observed with the latter sample, which implies that this carbonate species is associated with Ag–Cs sites, as discussed later. After a purge, the band at 2052 cm^{-1} disappeared, one at 2018 cm^{-1} remained, and the relative intensity of the band at 1953 cm^{-1} increased. The 2018 cm^{-1} band is presumably the counterpart to that at 2022 cm^{-1} with the UNP-II catalyst, but the Cs produced a small red shift, as discussed later. After reduction at 673 K and exposure of CsN (1175) to 10 kPa CO, the band intensities attributed to Cs carbonate species were lower compared to those after a 473 K reduction, and the band at 1507 cm^{-1} was not present. On the other hand, the band intensity in the region 1950–2055 cm^{-1} increased and a new band at 1883 cm^{-1} appeared (Fig. 9b), which was probably due to CO adsorbed on partially reduced cesium oxides or Ag atoms strongly affected by the Cs, because large red shifts for CO adsorbed on K-covered Pt (111) have been reported [32]. The bands at 2053 and 2038 cm^{-1} can be attributed to CO adsorbed on Ag sites, and the bands at 2026 and 1951 cm^{-1} may have contributions from CO coordinated with both Ag and reduced Cs oxide sites. Following a purge, a band at 2009 cm^{-1} dominated while the 1883 cm^{-1} band shifted to 1859 cm^{-1} and became more distinct. The additional red shift in this band position, from 2018 cm^{-1} , compared to the 2033 cm^{-1} band on unpromoted Ag, is attributed to the presence of Cs suboxides, which should be capable of donating more electrons to Ag than Cs_2O .

3.6. Cs,Cl–Ag/ α - Al_2O_3

Figure 10a displays spectra of CO adsorbed on CsCl (994) after reduction at 673 K, and they are similar to those obtained with CsN (1175). However, CsCl (994) reduced at 473 K exhibited absorption features different than those for

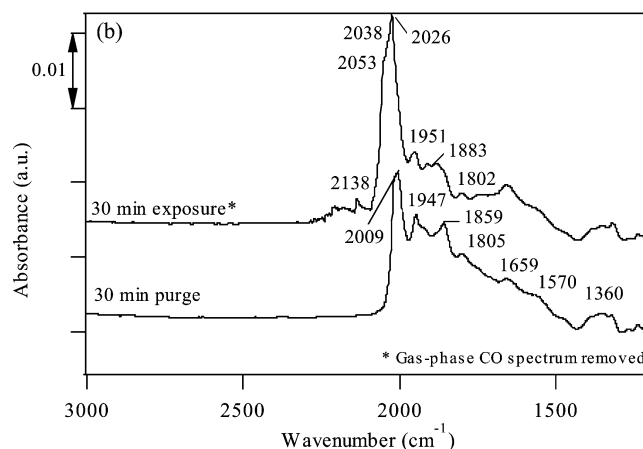
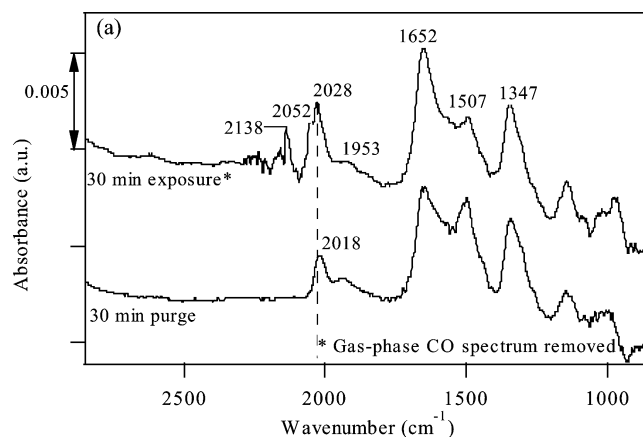


Fig. 9. DRIFT spectra of CO adsorbed on CsN (1175) at 300 K: (a) after a I-LT pretreatment; (b) after a I-HT pretreatment; $P_{\text{CO}} = 10$ kPa.

other supported silver catalysts, as demonstrated in Fig. 10b. Under 10 kPa CO, a dominant band developed at 2129 cm^{-1} along with bands at 2180, 2058, and 2022 cm^{-1} ; but all these bands disappeared after purging. At this time we do not know the reason for the loss in absorbance around 1670 cm^{-1} .

3.7. O-covered Ag/ α - Al_2O_3 catalysts

The spectra of the CO adsorbed on the catalysts subjected to a II-LT pretreatment exhibited only weak residual peaks after the gas-phase CO spectrum was removed (not shown here) [27]. Spectra for CO adsorbed on different catalysts at 300 K after a II-HT pretreatment are shown in Fig. 11. No band attributable to CO adsorbed irreversibly on alumina was observed because the band at 1642 cm^{-1} was due to the chemisorbed H_2O and it was observed regardless of the pretreatment. DRIFT spectra after CO adsorption on O-covered UNP-II (II-HT) exhibited very weak bands at 1593, 1505, and 1407 cm^{-1} , as shown in Fig. 11a, and, in addition, gas-phase CO_2 provided the doublet at 2348 cm^{-1} , thus indicating that chemisorbed oxygen on silver can react with CO. This feature was not observed with CsN (1175) and CsCl (994), apparently because any CO_2 that formed

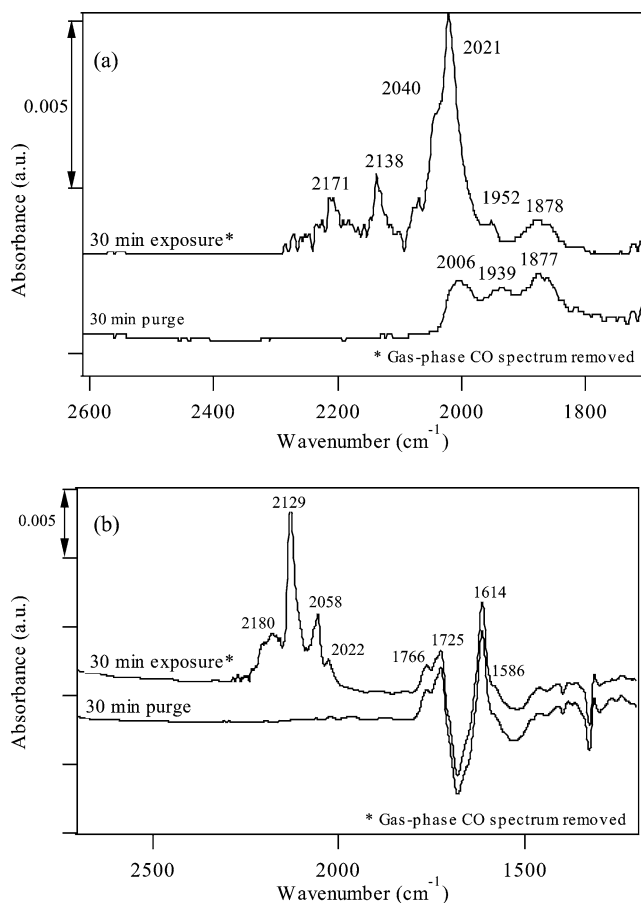


Fig. 10. DRIFT spectra of CO adsorbed on CsCl (994) at 300 K: (a) after I-HT pretreatment; (b) after I-LT pretreatment; $P_{\text{CO}} = 10$ kPa.

reacted rapidly with Cs oxide to form carbonates which gave absorption peaks around 1652 and 1340 cm^{-1} . After a II-HT pretreatment, CsN (1000, no silver) gave a broad band at 1660 cm^{-1} and a 1593 cm^{-1} shoulder due to Cs carbonate species. For Cs-promoted Ag catalysts, a dominant band around 1500–1520 cm^{-1} with a shoulder near 1490 and another band near 1348 cm^{-1} were observed in addition to the bands attributed to the Cs carbonate. Purging did not alter these bands significantly. The irreversible CO uptake on O-covered UNP-II (II-HT) was 0.9 $\mu\text{mol CO/g cat}$, which is higher than that on clean UNP-II. This suggests that the extinction coefficient for silver carbonate is lower than that for CO species adsorbed on silver.

4. Discussion

In this study, chemisorbed CO species on reduced, supported Ag catalysts were observed, and the nature of adsorption sites on both unpromoted and promoted Ag catalysts was investigated. Typical C_2H_4 epoxidation catalysts are extremely poor for 1,3-butadiene epoxidation, and these epoxybutene catalysts with high Cs loadings are very poor C_2H_4 epoxidation catalysts [4,5]; thus the information ob-

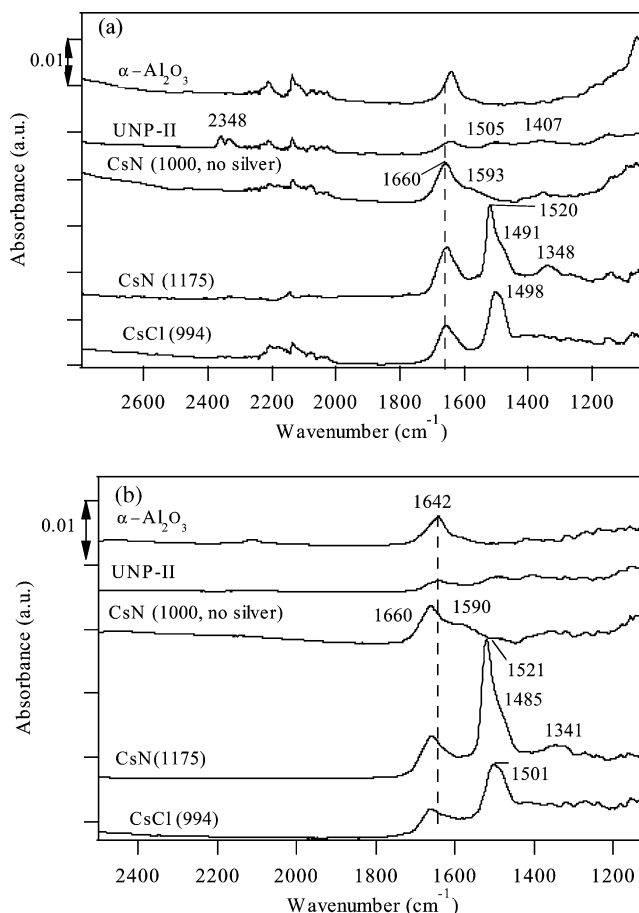


Fig. 11. DRIFT spectra of CO adsorbed at 300 K after applying II-HT pretreatment; (a) after a 30 min CO exposure (gas-phase CO spectrum removed); $P_{\text{CO}} = 10$ kPa; (b) after a 30 min purge.

tained here is examined primarily in regard to butadiene epoxidation. CO adsorption on reduced and O-covered silver catalysts, as well as on unsupported silver powder, gave rise to various species which exhibited IR absorption bands in the 1300–1700 cm^{-1} and 1870–2140 cm^{-1} spectral regions, as tabulated in Table 4. As displayed in Figs. 3 and 4, CO adsorption on unpromoted $\text{Ag}/\alpha\text{-Al}_2\text{O}_3$ at 10 kPa and 300 K gave bands at 2028 and 2048 after reduction at 473 K and at 2040 and 2055 cm^{-1} after reduction at 673 K, which represent linearly adsorbed CO on metallic Ag atoms with different coordination numbers, as well as a band near 1960 cm^{-1} due to bridge-bonded CO [28,29,33]. The DRIFTS results are also consistent with adsorption measurements showing that the CO uptake is very small, but discernible on a clean UNP-II catalyst, as addressed later when the pressure dependency of CO adsorption is discussed. A study by Pearce showed similar CO adsorption behavior on SiO_2 -supported Ag, i.e., a band at 2060 cm^{-1} with a shoulder at 2015 cm^{-1} was formed, and after evacuation the latter band intensified, the former band was removed, and a new band at 1884 cm^{-1} was formed which was assigned to bridged CO species [34]. All other previous studies with supported silver catalysts consistently

Table 4
Infrared band assignments for CO adsorbed at 300 K on different catalysts

Sample	Pretreatment	Linearly bonded CO (cm ⁻¹)	Bridged bonded CO (cm ⁻¹)	Carbonates (cm ⁻¹)
UNP-II	I-LT	2048, <u>2028</u>	1953	
	I-HT	<u>2055</u> , 2040	1962	
	II-HT	–	–	1593, 1505, 1407
Ag Powder	I-LT	2056, <u>2046</u>	1952	–
	II-LT	–	–	–
CsN (1000, no Ag)	I-LT	–	–	
	I-HT	2028, <u>1950</u> , <u>1869</u>		1660, 1593, 1360
	II-HT	–		<u>1660</u> , 1593, 1360
CsN (1175)	I-LT	2052, 2028, 2018	1953	<u>1652</u> , 1507, 1347
	I-HT	2053, 2038, <u>2026</u> , 2009	1951–1947, 1883,	1660, 1570, 1360
	II-HT	–	–	1660, <u>1520</u> , 1348
CsCl (994)	I-LT	2180, <u>2129</u> , 2058, 2022	–	1614, 1586
	I-HT	2040, <u>2021</u> , 2006	1952, 1878	–
	II-HT	–	–	1660, <u>1498</u>

More intense bands after CO exposure are underlined.
Refs. [28,29,31].

reported no detectable IR bands for irreversibly adsorbed CO on metallic silver, as shown in Table 5. Keulks and Ravi found that CO adsorption at room temperature on Ag/SiO₂ or Ag/ γ -Al₂O₃ after a 2-h reduction in H₂ at 423–448 K gave no band [17]. Similarly, CO adsorption on Ag dispersed on three different supports did not give any discernible IR peak at either 300 or 123 K after reduction by CO between 373 and 673 K [18]. Huang reported that after Ag-exchanged X and Y zeolites were reduced at 623 K under flowing CO, exposure to CO at 300 K gave rise to no bands [19]. In these earlier studies, no calcination step was conducted be-

fore reduction. However, it has been found that a reduction treatment alone, even at 773 K, may not sufficiently clean the silver surface, and only a calcination/reduction cycle gave a clean surface as well as reproducible chemisorption behavior [35].

In contrast to studies using only a reduction step, Hadjiivanov and Knözinger studied CO adsorption on samples of Ag-ZSM-5 and Ag/SiO₂ after calcination at 673 K and observed bands around 2190 cm⁻¹, but no bands around 2060 cm⁻¹, which indicated the absence of reduced silver sites [20,21]. Although Akolekar and Bhargava reported

Table 5
IR band positions for CO adsorbed on supported Ag

Support	Adsorption site	T (K)	P (Torr)	Frequency (cm ⁻¹)	References
SiO ₂	Ag ^{0a}	RT	20	No band	[17]
	Ag ^{+b}	RT		2180 ^e	
γ -Al ₂ O ₃	Ag ^{+c}	RT		No band	[18]
	Ag ^{0d}	RT, 123	NA	No band	
γ -Al ₂ O ₃ Aluminasilicate	Ag ^{+b}	RT		2175 ^e 2175 ^e , 2195 ^e	[19]
	Ag ^{+b}	RT	53	2195 ^f	
AgX			55	2195 ^e	[20]
ZSM-5	Ag ^{+b}	RT 220	4–64	2189–2192 ^f 2189, 2195	
SiO ₂		RT	12	2189, 2169 ^e	[21]
ZSM-5	Ag ^{+b}	RT	6	2191 ^f	
ZSM-5	Ag ^{+b}	296	12–61	2190	[22]
	Ag ^{0a}			2140	

^a Pretreated with H₂.

^b Pretreated with O₂ higher than RT.

^c Pretreated with O₂ at RT.

^d Pretreated with CO.

^e Under P_{CO}.

^f After purging, intensity decreased to some extent.

that CO adsorption on Ag-ZSM-5 at 296 K gave a band at 2140 cm^{-1} , which they assigned to CO adsorbed on metallic silver [22], our present study (and others) shows that this peak should be assigned to CO on partially oxidized silver rather than Ag^0 . For example, CO adsorption on the LT-treated Ag powder gave bands at 2046 and 2056 cm^{-1} , which correspond to CO adsorbed on metallic Ag atoms, and a band at 2140 cm^{-1} was also observed, which can be assigned to CO adsorbed on partially oxidized silver sites. To further explain the earlier incapability to observe IR bands for CO adsorbed on reduced Ag, the CO pressure must also be taken into account. In these earlier studies, CO was present at 2.6 to 7.2 kPa [17–19] and, as discussed later, CO adsorption behavior on silver appears to be pressure-dependent. Moreover, the presence of water vapor may affect CO adsorption because Hadjiivanov showed that exposure of Ag-ZSM-5 covered with preadsorbed CO to 0.5 kPa H_2O vapor (5200 ppm) strongly decreased the CO band intensity [20]. Thus it appears that the pretreatment, the extent of surface contamination, the adsorption pressure and temperature, the support, the gas purity, and surface morphology can affect CO adsorption on dispersed Ag crystallites.

Unlike supported Ag catalysts, CO adsorption on Ag films has given rise to bands assigned to CO adsorbed on metallic Ag sites [9–16], as shown in Table 6. Except for one study carried out at 300 K, CO adsorption on Ag films was conducted at subambient temperatures, and band positions fall into the 2160 to 1932 cm^{-1} spectral region but varied from one study to another. Vibrational spectroscopy techniques have not been widely used to study CO adsorption on single silver crystals, but HREELS and RAIRS results for Ag (111) are also displayed in Table 6. CO adsorption on clean Ag (111) after an exposure of 3300 L produced no detectable CO stretching mode at 77 K (7). Hansen et al. observed a band at 2137 cm^{-1} for CO adsorbed on Ag (111) at temperatures below 35 K, and this band

intensity increased as the CO exposure increased from 2 L to 8 L [8].

CO adsorption on the unpromoted Ag catalyst was examined at pressures up to 80 kPa to determine the pressure dependency after either the I-LT or the HT pretreatment (Figs. 5a and 6a). As the pressure increased, the absorption intensities also increased, regardless of the pretreatment, which indicated that the Ag surface was not saturated with CO. This was verified by volumetric measurements which showed that monolayer coverage was not reached even at CO pressures as high as 57 kPa. Using oxygen uptakes to count the number of surface silver atoms, CO coverages on the silver surface after different reduction pretreatments were determined assuming that the limiting stoichiometric ratio of $\text{CO}_{\text{ad}}/\text{Ag}_s$ is unity (Ag_s is a surface Ag atom). Thus, after exposure of a clean UNP-II sample to 9.2 kPa CO at 300 K, CO covered only 3–3.7% of the Ag_s atoms, and at a higher pressure of 53 kPa, CO covered only 3.0% or 7.0% of the Ag_s atoms after either a I-LT or a I-HT pretreatment, respectively. Thus even though the CO uptake changes, monolayer coverages of CO are not reached after any of the different pretreatments and adsorption pressures used here. This is in accordance with previous UHV studies showing that CO adsorbs very weakly on silver, and either low temperatures or high pressures are required to achieve significant CO coverages [36–38], although pressures considered high in such studies are low compared to those used here. The pressure dependency of CO adsorption on a silver film at 113 K has been examined, and a band at 2160 cm^{-1} due to adsorbed CO was visible between 9×10^{-5} and 9×10^{-3} kPa [9]. In the same manner, Wood and Klein observed an increase in the band intensity due to the CO stretching mode as the pressure increased from 1.3×10^{-10} to 1.3×10^{-4} kPa during CO adsorption on a Ag film at 105 K, as well as a shift in the band position from 2145 to 2134 cm^{-1} [15].

Table 6
CO adsorption bands on Ag single crystals and films

Silver form	Temperature (K)	Vibrational spectroscopy ^a	Frequency (cm^{-1})	Reference
Ag (111)	77	RAIRS	No band	[7]
Ag (111)	< 35	HREELS	2137	[8]
Film	113	IR	2160–2150 depending on the coverage	[9]
Film	2	IR	2148	[10]
	2		2143	
Island films	17	SERS	2112	[11]
			2139	
Film (99.99%)	300	SERS	2112	[12]
		IR	1940	
Film	78	Raman	2070, 1995	[13]
Film	120	SERS	1860–2200	[14]
Film (99.999%)	105	SERS	2135 (Under CO)	[15]
			2118, 1932 (After evacuation)	
Foil	90	RAIRS	2060	[16]
	heat to 300 K, cooled to 85 K		~2037, 1950	

^a RAIRS—reflection–absorption infrared spectroscopy; HREELS—high-resolution electron energy loss spectroscopy; SERS—surface enhanced Raman spectroscopy.

After CO adsorption at 10 kPa following reduction at 473 or 673 K, a purge removed the respective absorption peaks at 2048 and 2055 cm^{-1} (Figs. 5b and 6b); however, at pressures of 40 kPa and above, those peaks remained dominant, although their position was slightly red shifted. Moreover, after CO adsorption at pressures below 40 kPa, purging with He resulted in an increase in intensity near 1953–1962 cm^{-1} , which indicates that binding in a bridged-bonded form is favored during purging. However, after CO adsorption at higher pressures, no significant increase in the intensity of the bridged-bonded band was observed, which suggests that, at exposures to high CO pressures, linearly adsorbed CO forms which is stable and covers the binding sites involved in the formation of bridged-bonded CO.

It should be also pointed out that as the adsorption pressure of CO was increased, new bands developed at 2016 and 2024 cm^{-1} , especially with the UNP-II catalyst reduced at 673 K. The effect of CO pressure has been investigated with Pt (111) at 300 K, and at CO pressures up to 92 kPa, a new, broad band at 2045 cm^{-1} was observed [39,40]. Based upon scanning tunneling microscopy (STM) results, it was proposed that some Pt atoms could be pulled from the crystal lattice at high CO pressures to produce step or kink sites, thus providing different adsorption sites for CO [39,40]. Consequently, it may be that during CO adsorption on Ag at high CO pressures reconstruction of the Ag surface can also occur.

Oxygen uptakes have been previously measured on a Ag/SiO₂ catalyst after the application of one of two pretreatments, i.e., calcination at 773 K followed by reduction in H₂ at either 573 or 673 K, and the oxygen uptake after the higher reduction temperature was almost 10% higher than that after reduction at 573 K [35]. Our results also show that the reduction temperature can have an effect on adsorption capacity, and the oxygen uptake, which represents the Ag_s concentration in these silver catalysts, was 4.6 μmol “O”/g cat for the unpromoted catalyst after a I-LT pretreatment and 5.6 μmol “O”/g after a I-HT pretreatment. This indicates that adsorption sites for oxygen increased by over 20% after reduction at 673 K. Furthermore, IR results demonstrated that bands due to adsorbed CO are narrower and their intensity is higher for UNP-II subjected to a I-HT pretreatment compared to those obtained after a I-LT pretreatment. Bandwidth typically decreases as the ordering increases [41]; therefore, this may imply that surface homogeneity increases after a I-HT pretreatment, presumably due to removal of more oxygen and surface restructuring [35]. Similarly, Nagy et al. reported that silver undergoes pronounced morphological changes following a high-temperature treatment in oxygen which led to faceting of the silver surface as indicated by SEM analysis [42]. Consequently, in the present study, the reduction temperature of 673 K may be just high enough to remove some of these oxygen atoms but low enough to allow step, kink, and terrace sites to remain, therefore exposing different adsorption sites to CO.

CO isotherms were measured on UNP-II after reduction at either 473 or 673 K, as shown in Fig. 7, and the spectra in Figs. 5 and 6 can also be represented in terms of Kubelka–Munk units, which allows intensities to be quantitatively related to uptakes, as described elsewhere [41,43–47]. For an “infinitely thick” sample, the Kubelka–Munk function can be expressed as

$$f(R_\infty) = \frac{(1 - R_\infty)^2}{2R_\infty} = \frac{k}{s}, \quad (1)$$

where R_∞ is the absolute reflectance spectrum of the sample referenced to that of a background spectrum (preferably nonabsorbing), s is a scattering coefficient, and k is the molar absorption coefficient of the adsorbate, which can be expressed in terms of the extinction coefficient of the absorbing compound as

$$k = 2.303\varepsilon C, \quad (2)$$

where ε is the extinction coefficient and C is the concentration of this component. Equation (2) predicts a linear relationship between the intensity at a given frequency, i.e., $f(R)$, and the concentration, C , with a zero y -intercept if the scattering coefficient remains constant. Based on the isotherms, the Kubelka–Munk intensity of the predominant band at each pressure was plotted versus CO uptake on UNP-II after reduction at either 473 or 673 K, as shown in Fig. 12. The slope is equal to 2.303 ε/s , and if the extinction coefficient is known, one can estimate the scattering coefficient, s , which can vary with the particle size of the adsorbent. Although the extinction coefficient values for metal–CO complexes can differ significantly depending on the $\nu(\text{CO})$ value, and ε tends to increase as the $\nu(\text{CO})$ frequency decreases, Davydov et al. [48] have reported that the extinction coefficient for Ag⁺–CO complexes was 0.36 $\text{cm}^2/\mu\text{mol}$ (for the 2170 cm^{-1} band). Thus ε may be higher in our study than this reported value; however, this ε value is the same as that reported for linearly adsorbed CO on Pd [49]. Using this ε value, scattering coefficients of 330 cm^{-1} and 200 cm^{-1} were calculated for the LT- and HT-treated UNP-II catalysts, respectively, and these values are lower than that of 900 cm^{-1} reported for a Cu/ η -Al₂O₃

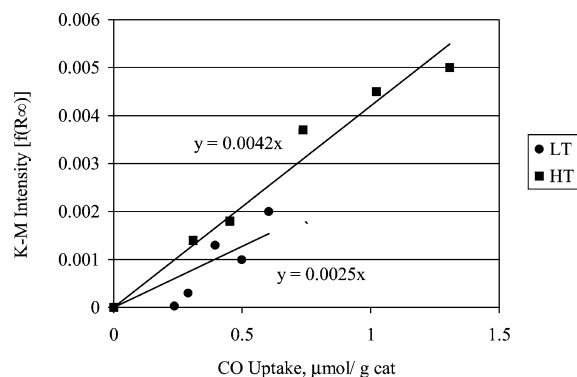


Fig. 12. Variation in the Kubelka–Munk intensity of CO adsorbed on Ag⁰ as a function of Ag⁰ surface concentration.

catalyst [50]. The s_{LT}/s_{HT} ratio was 1.7, which implies that the scattering coefficient depends somewhat on the pretreatment and is consistent with the proposition that crystallite restructuring or redispersion may occur during the pretreatment steps [34], thus affecting s in these catalysts with high Ag loadings.

To examine the effect of cesium, experiments were carried out not only with Cs-promoted Ag catalysts, but also with a 0.1% Cs/ α -Al₂O₃ sample, i.e., CsN (1000, no Ag). After a I-LT-pretreatment, this sample provided no bands due to adsorbed CO (see Fig. 8); however, after a I-HT pretreatment, CO adsorption gave distinct bands at 2028, 1950, 1869 cm⁻¹ in addition to weaker bands at 1660, 1593, and 1360 cm⁻¹ (Fig. 8). For transition metals, bands in the region 2028–1869 cm⁻¹ are typically assigned to CO adsorbed on metallic sites, but this generalization does not apply to pure alkali metals. However, CO adsorption on metals partially covered with an alkali metal typically gives bands at low frequencies, i.e., below 1700 cm⁻¹, at high alkali metal coverages [32]. In our current study, bands in the 1660–1360 cm⁻¹ range were observed, but these bands are attributed to Cs carbonate species [31] because similar bands were obtained with the O₂-treated samples. In addition, Rodriguez et al. have provided evidence for carbonate formation in Cs-covered Cu systems [51]. For this reason, Cs/ α -Al₂O₃ was subjected to a third, different pretreatment, i.e., calcination at 773 K as in the I-HT pretreatment, but reduction at 473 K as in the I-LT pretreatment. After CO adsorption on this sample, no bands in the spectral region 2028–1869 cm⁻¹ were observed and only bands in the region 1660–1360 cm⁻¹ occurred (see Fig. 13), indicating that the reduction temperature is important in the formation of reduced cesium oxides. The possibility of reducing some types of Cs oxide under pretreatment conditions was also examined, and the Gibbs free energies and enthalpies of formation at 298 K for four different Cs oxides [52,53] were used to calculate values at 473 and 673 K [27], which are listed in Table 7. Reduction at either 473 or 673 K is thermodynamically unfavorable only for Cs₂O and, because no bands due to CO adsorption on Cs were observed after a I-LT pretreatment, it is assumed Cs₂O is the principal Cs oxide present at 473 K. However, the equilibrium concentration of water is 0.02 ppm at 473 K and 53 ppm for reduction at 673 K; consequently, in a continuous flow of high purity H₂ in He, some Cs₂O may be reduced at 673 K to cesium suboxides such as Cs₃O, Cs₄O, Cs₇O. This possibility is consistent with the study of Kim et al., who showed that Cs₂O heated to temperatures above 623 K in an inert atmosphere decomposed to Cs₇O [54]. Furthermore, Bukhtiyarov and co-workers studied Cs–O complexes on Ag (111), Ag (110), and alumina-supported Ag surfaces utilizing XPS, and Cs peroxide and Cs suboxides were commonly observed at 420 K [55,56]. Under our pretreatment conditions, the presence of Cs peroxide was ruled out, so it is hypothesized

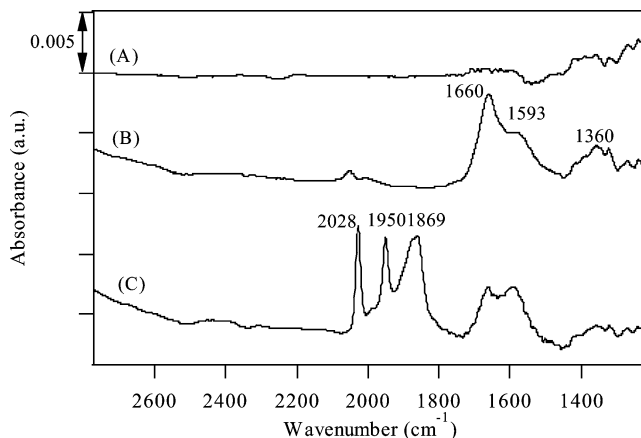


Fig. 13. DRIFT spectra of adsorbed CO on CsN (1000, no silver) at 300 K: (A) after I-LT pretreatment; (B) calcination at 773 K, reduction at 473 K, (C) after I-HT pretreatment.

that the observed bands are primarily due to CO adsorption on cesium suboxides.

After CO adsorption on the Cs-promoted Ag catalyst subjected to either a I-LT or a I-HT pretreatment, similar bands were observed (Figs. 9a and 9b). The band observed at 1507 cm⁻¹ after reduction at 473 K was also observed on CsN (1175) after either a II-LT or II-HT pretreatment, which implies that this adsorption site, which will be discussed later, was not reduced at 473 K. The bands at 2054 and 2028 cm⁻¹ are associated with CO adsorbed on metallic Ag sites, while the bands at 2026, 1951, and 1883–1873 cm⁻¹ are attributed to CO adsorption on Cs suboxides or Ag atoms strongly interacting with the Cs promoter. Similar red shifts in the CO spectrum have been reported for CO adsorbed on K- and Cs-promoted Pd on SiO₂ [57]. There has been a substantial effort to better understand the interaction between alkali metals and various adsorbates [32,51,57–60]. The general conclusion from these studies has been that two kinds of adsorption sites exist, i.e., one type affected by the alkali metal and the other type remaining like a clean metal site. In our study, CO adsorption on Cs-promoted Ag catalysts showed bands which are attributed to CO adsorbed on both Cs and Ag sites. In addition to these bands, two others at 2018 and 2009 cm⁻¹ were observed on CsN (1175) samples reduced at 473 K and 673 K, respectively. These bands were red-shifted compared to those observed on unpromoted Ag/ α -Al₂O₃, and this indicates that CO adsorption on Cs-promoted silver catalysts occurred not only on unaffected Ag

Table 7

Gibbs free energy of formation for the reduction of cesium oxides at 473 and 673 K

Reaction	ΔG_{f473}^0 (kcal/mole Cs)	ΔG_{f673}^0 (kcal/mole Cs)
$\text{Cs}_2\text{O}_{(s)} + \text{H}_2_{(g)} \rightarrow 2\text{Cs}_{(s)} + \text{H}_2\text{O}$	7.5	5.5
$\text{Cs}_2\text{O}_{2(s)} + 2\text{H}_2_{(g)} \rightarrow 2\text{Cs}_{(s)} + 2\text{H}_2\text{O}$	-16.2	-18.8
$\text{Cs}_2\text{O}_{3(s)} + 3\text{H}_2_{(g)} \rightarrow 2\text{Cs}_{(s)} + 3\text{H}_2\text{O}$	-39.1	-41.9
$\text{CsO}_{2(s)} + 2\text{H}_2_{(g)} \rightarrow \text{Cs}_{(s)} + 2\text{H}_2\text{O}$	-61.7	-65.9

sites (this CO disappeared after a 30-min purge) but also on Ag sites affected by the Cs (this CO remained after a 30-min purge). Rodriguez et al. have also reported the formation of a Cs–CO complex on Cu that increases the CO heat of adsorption [51]. After eight I-HT pretreatments, 20% of the Cs had been removed from the catalyst and the principal band had shifted back to 2020 cm^{-1} , consistent with a decreased electronic effect [27].

After CO adsorption on I-HT-pretreated CsCl (994), bands similar to those with CsN (1175) were present, presumably because most of the Cl was removed from the surface by the high-temperature calcination and reduction steps (Fig. 10a); however, CO adsorption on CsCl (994) after reduction at 473 K produced a dominant band at 2129 cm^{-1} as well as bands at 2180, 2058, and 2022 cm^{-1} (Fig. 10b). The latter two bands are due to CO adsorbed on metallic Ag sites and the band at 2180 cm^{-1} is attributed to CO adsorption on oxidized Ag sites based on earlier studies which have reported ionic Ag^+ –CO complexes which give bands in the spectral region 2170–2180 cm^{-1} [17–22]. The band at 2129 cm^{-1} is at a lower frequency than bands due to a Ag^+ –CO complex and at a higher frequency than bands due to Ag^0 –CO species; consequently, it is attributed to Ag sites in contact with Cl. The presence of an electron-withdrawing Cl atom may induce a partially empty *d*-band and could change the electronic structure of surface Ag atoms [2]. Jørgensen and Hoffmann and van den Hoek et al. reported that $\text{Ag}^{\delta+}$ atoms were formed by charge transfer to subsurface chlorine or oxygen atoms [61,62]. Furthermore, Frank and Hamers suggested that chlorine induced microfaceting of Ag (111) to give a different step/terrace distribution, and $\text{Ag}^{\delta+}$ sites were formed by electron smoothing at step edges and microfacets [63]. After a purge, all bands associated with CO disappeared, indicating weak adsorption of CO on the Cl-promoted Ag catalysts (Fig. 10b).

On all catalysts subjected to a II-HT pretreatment, no bands in the spectral region 1800–2060 cm^{-1} were observed, which further supports the conclusion that the sites

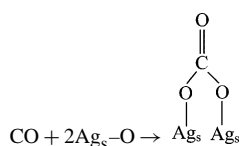
responsible for these bands are associated with reduced forms of silver and cesium oxides. CO adsorption on supported Ag catalysts has produced bands around 2195–2175 cm^{-1} attributed to a Ag^+ –CO complex, as shown in Table 5. In our study, however, no band in this region was observed; instead a clean-off reaction, i.e., $\text{CO}_{(\text{g})} + \text{O}_{(\text{a})} \rightarrow \text{CO}_{2(\text{g})}$, occurred along with the adsorption of CO_2 to form carbonate species. This reaction has been reported by several authors [38,64–67] to occur on O-covered Ag surfaces between 160 and 310 K. Bowker et al. also suggested that at high oxygen coverages, incomplete removal of adsorbed O atoms may occur due to the readsorption of CO_2 , which can form silver carbonate [38]. Several investigations have found that no CO_2 adsorbed on a clean Ag surface at 100 or 300 K, whereas on an O-covered silver surface, carbonate formation occurred [64,66]. In our study, weak bands at 1593, 1505, and 1407 cm^{-1} were observed on the UNP-II catalyst, which might be due to unidentate and bidentate silver carbonate species [68]. CO uptakes on O-covered UNP-II and O uptakes on the reduced catalyst are tabulated in Table 8. Assuming that CO reacts on a O-covered Ag surface to give $\text{CO}_{2(\text{g})}$ and $\text{CO}_{2(\text{g})}$ adsorbs on Ag sites to give bidentate Ag carbonate, which gives a maximum coverage, carbonate coverages were calculated to be around one-third, indicating that complete coverage on O-covered UNP-II cannot be attained, regardless of the pretreatment. Again, as on a clean Ag surface, CO adsorption appears to take place on only a limited portion of the Ag surface, although CO uptake values are higher than that on the clean surface.

CO adsorption on Cs/ α - Al_2O_3 after any pretreatment exhibited bands due to bidentate carbonates, which have asymmetric stretching bands near 1595–1630 cm^{-1} and stretching symmetric bands around 1320–1340 cm^{-1} , thus giving an overall splitting of about 300 cm^{-1} , as reported by Doscocil and Davis [31]. On the Cs-promoted Ag catalysts, however, additional bands at 1520 and 1491–1498 cm^{-1} were observed, which may be due to a unidentate carbonate species. A similar band at 1507 cm^{-1} was observed on CsN (1175) reduced at 473 K, but these strong bands did

Table 8
O₂ and CO adsorption on the UNP-II catalyst

Pretreatment	O ₂ Uptake at 443 K ($\mu\text{mol O/gcat}$)		Pretreatment	CO Uptake at 300 K ($\mu\text{mol CO/gcat}$)		$2\text{CO}_{\text{irr}}^{\text{a}}/2\text{O}_{2\text{irr}}^{\text{b}}$
	Rev.	Irrev.		Rev.	Irrev.	
I-LT	0	2.3	II-LT	0.1	0.7	0.30
I-HT	0	2.8	II-HT	0.5	0.9	0.32

^a Based on



(assuming bidentate carbonate formation).

^b Based on $2\text{Ag}_s + \text{O}_2 \rightarrow 2\text{Ag}_s\text{-O}$.

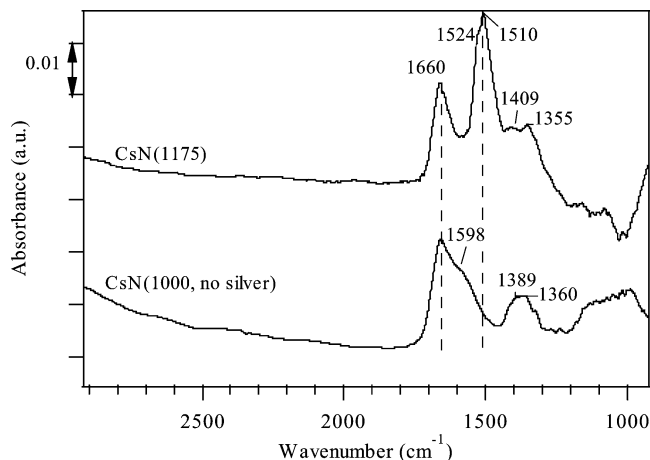


Fig. 14. DRIFT spectra of CO_2 adsorbed at 300 K after applying II-HT.

not exist on UNP-II or $\text{Cs}/\alpha\text{-Al}_2\text{O}_3$. Especially on the II-HT-pretreated samples, these bands are dominant and remain after purging. One can argue that on CsN (1175), the presence of Ag facilitates gas-phase CO_2 formation; thus additional Cs carbonate may be formed on the surface. In an effort to verify this, CO_2 adsorption was conducted on both $\text{Cs}/\alpha\text{-Al}_2\text{O}_3$ and CsN (1175) (Fig. 14). If additional CO_2 led to formation of this carbonate species, it would be expected to see this band after CO_2 adsorption, but no band in this region was observed with $\text{Cs}/\alpha\text{-Al}_2\text{O}_3$. In contrast, CO_2 adsorption on the Cs-promoted Ag catalyst produced bands at 1520 and 1490 cm^{-1} similar to those after CO adsorption. Because the latter bands were not observed on $\text{Cs}/\alpha\text{-Al}_2\text{O}_3$, this suggests that oxygen atoms may coordinate with both Cs and Ag atoms to form a AgCs_xO_y surface complex [69]. Grant and Lambert have proposed that oxygen might induce a Ag–Cs mixed surface oxide complex [70], which cannot be formed in the absence of oxygen [71]. This may explain the band at 1507 cm^{-1} on CsN (1175) because the I-LT pretreatment was not as efficient as the I-HT pretreatment in removing oxygen from the surface and Cs_2O cannot be

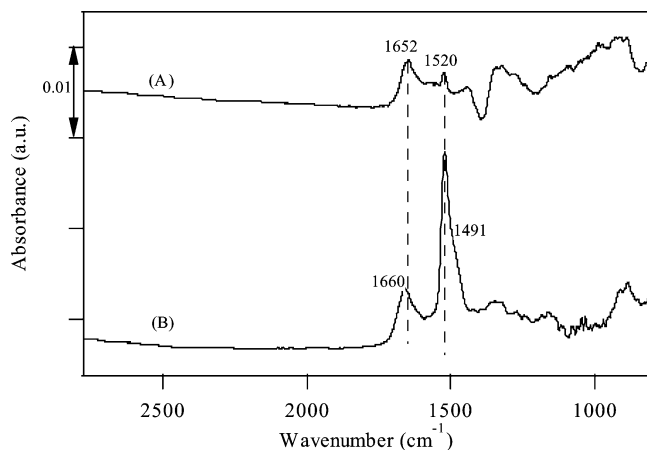


Fig. 15. Comparison of DRIFT spectra taken for CsN (1175) at 300 K: (A) after a II-LT pretreatment; (B) II-HT pretreatment.

reduced to cesium suboxides; therefore, carbonate species were formed at mixed Cs–Ag sites, giving the 1507 cm^{-1} band. Thus on O-covered Ag surfaces Cs carbonates and Cs–Ag carbonates are found on the Ag catalysts in addition to gas-phase CO_2 formation.

Figure 15 provides a comparison of two spectra taken for CsN (1175) at 300 K after either a II-LT or a II-HT pretreatment. The intensity of the band at 1520 cm^{-1} , which is assigned to a COO^- stretching mode of monodentate carbonates formed on Ag–Cs mixed oxide sites [6], was much greater for the sample subjected to the II-HT pretreatment. Although scattering coefficients might be different for the LT- and HT-pretreated CsN (1175) samples, this increase may be explained by the fact that HT pretreatment increased the mobility of Cs, which can lead to surface structures in which domains of Ag are separated by Cs; as a result, oxygen introduction leads to an increase in AgCs_xO_y site formation. Since it was shown that butadiene adsorbs via both C=C bonds with one site being unpromoted Ag and the other AgCs_xO_y [72], pretreatment dependency may play an important role on tailoring the catalyst for better activity and selectivity. This evidence for two types of adsorption sites on Cs promoted $\text{Ag}/\alpha\text{-Al}_2\text{O}_3$ catalysts is consistent with the proposal by Monnier that a dual-site reaction mechanism best explains the kinetic behavior for butadiene epoxidation over these systems [4].

5. Summary

Supported and promoted silver catalysts were characterized by DRIFT spectra of CO adsorbed at 300 K on their surfaces after different pretreatments. A small extent of molecular CO adsorption occurred on Ag^0 sites after a calcination step and reduction at either 473 or 673 K, and these surface species gave bands between 2055 and 2006 cm^{-1} . This CO adsorption occurred on less than 10% of the total Ag surface and depended on the pretreatment and CO pressure utilized, thus CO does not adsorb stoichiometrically on surface Ag atoms, which implies that CO adsorbs irreversibly only on higher index planes containing Ag_s atoms with low coordination numbers. In fact, after a I-HT pretreatment, which may result in surface reconstruction, the intensity of CO adsorbed on metallic Ag^0 sites increased, and after exposure of a reduced, unpromoted Ag catalyst to high pressures of CO, which may also possibly result in surface restructuring to form step and kink sites, new bands became visible. In the presence of a Cs promoter, CO adsorbed not only on silver sites, but also on sites presumed to occur on Cs suboxides, especially after reduction at 673 K.

After a purge, the bands due to linearly adsorbed CO decreased in intensity, while bands due to bridge-bonded CO increased in intensity for the reduced samples exposed to 10 kPa of CO, which indicates that CO molecules reorient themselves as their surface concentration decreases, and similar behavior occurred when Cs was present. In addition,

bands at 2018 and 2009 cm^{-1} became visible, which were attributed to CO adsorption on Ag sites electronically affected by Cs after reduction. Subjecting Cs-promoted Ag catalysts to consecutive high-temperature pretreatments resulted in the removal of some Cs from the catalyst [27].

On a CsCl-promoted Ag catalyst, a dominant band appeared at 2129 cm^{-1} after reduction at 473 K due to CO adsorbed on an ionic form of silver, $\text{Ag}^{\delta+}$. CO adsorption on $\text{Ag}^{\delta+}$ sites was reversible at 300 K and after a 30-min purge no bands remained on this sample; however, after reduction at 673 K, both the Cs-only-promoted and CsCl-promoted catalysts exhibited similar bands, which implies that Cl can be removed from the surface during the high-temperature pretreatments.

After monolayer O coverages on Ag were established by O_2 adsorption at 443 K, exposure of these supported Ag catalysts to CO at 300 K removed some of the chemisorbed oxygen via gas-phase CO_2 formation. This process also resulted in carbonate formation, and both Ag and Cs carbonate species were detected. Bands at 1507, 1520, and 1490–1498 cm^{-1} were present on Cs-promoted catalysts after any pretreatment except the I-HT pretreatment, which may indicate that oxygen induces the formation of a Ag–Cs mixed surface oxide complex, as suggested by others. More AgCs_xO_y sites appear to have been formed on the sample subjected to a II-HT pretreatment than that subjected to a II-LT pretreatment, and this was attributed to the redistribution of Cs atoms after a HT pretreatment.

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