

Adsorption of NO on promoted Ag/ α -Al₂O₃ catalysts

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Abstract

Nitric oxide was used to probe Ag/ α -Al₂O₃ epoxidation catalysts. NO dissociated on reduced silver catalysts to oxidize metallic silver sites and desorb N₂O at 300 K. Uptake measurements and DRIFTS results showed that Ag–O sites were the principal surface species formed after NO adsorption at 300 K on reduced, unpromoted Ag catalysts, as indicated by the formation of gas-phase N₂O as well as a value of unity for the NO/O uptake ratio. The formation of nitrite species was time dependent and a weak band due to chelating nitrito was observed after long exposure times for the unpromoted catalyst after reduction at 473 K. On the unpromoted, O-covered Ag surface, NO adsorption produced a band at 1396 cm⁻¹ which was assigned to a nitrate species. Bands at 1238 and 1345 cm⁻¹, assigned to chelating nitrito and nitrate species, respectively, were detected after NO adsorption on Cs-promoted Ag surfaces reduced at 473 K or covered with chemisorbed oxygen following reduction at 673 K. Only the 1238 cm⁻¹ band was observed after NO adsorption on the Cs-promoted catalyst following reduction at 673 K, and this band was the only absorption feature after NO adsorption on a Ag surface promoted with both Cs and Cl, regardless of the pretreatment. In the presence of Cs, all results indicated that the chemistry of oxygen at the Ag surface was different and more oxygen existed on the surface. The presence of surface oxygen enhanced NO_x adsorption, and the presence of both Cl and Cs may decrease the surface concentration of nucleophilic oxygen, which forms nitrate species. After O₂ and NO coadsorption on unpromoted Ag, the O₂ desorption peak was shifted 100 K higher to 660 K. When NO was adsorbed in the presence of gas-phase O₂, bulk Ag nitrate was a dominant species.

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1. Introduction

A better understanding of the adsorption behavior of oxygen and the effects of promoters on silver catalysts is crucial for gaining insight into epoxidation reaction mechanisms. CO has recently been used as a probe molecule to elucidate the oxidation states of Ag and the effects of Cs and Cl [1]. In the current study, NO was also used to probe the effect of promoters like Cs and Cl on the adsorption behavior of NO and O₂, as well as oxygen adsorption on unpromoted Ag surfaces. Previous studies have used an O₂ chemisorption–H₂ titration technique to determine the surface area and dispersion of silver in supported Ag catalysts [2–4]. If NO dissociatively adsorbs on Ag at 300 K and its adsorption does not lead to the formation of reactive NO_x products so that the process can be stoichiometrically described, then NO might also be used to count Ag sites.

The distribution of electrons in the NO molecule is similar to that in the CO molecule, with the main difference being that NO has one unpaired electron occupying the π^* orbital. Thus even slight changes in electron density due to NO adsorption result in a noticeable change in the frequency of NO stretching vibrations. The thermodynamic properties of NO ($\Delta G_{f, 298 K}^\circ = 20.7$ kcal/mol) indicate the potential instability of the molecule [5]. For most transition metals, it has been reported that the adsorption behavior of NO and CO is similar [6], whereas for silver it differs in a way that the heat of adsorption, Q_{ad} , is 5 kcal/mol for CO compared to 25 kcal/mol for NO, as reported by Behm and Brundle [6]. Most of the recent studies have been devoted to the investigation of NO_x reduction on Ag dispersed on γ -alumina [7–19], whereas previous surface science studies focused on NO_x adsorption on Ag single crystals, foils, or powders [20–40]. Contradictory results exist; for example, Lambert and co-workers have reported molecular NO adsorption at 300 K on the Ag (111) or Ag (110) surface [20–22], whereas the Ag (111) surface has been found to be unreactive with NO at

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295 K by others [26,34,37,38]. Surface science studies have reported that NO adsorption is structure sensitive, and temperature and pressure also affect its adsorption behavior. To date researchers have mainly focused on the interaction between NO and Ag at subambient temperatures, which has resulted in the formation of adsorbed (NO)₂ dimers and N₂O, as shown by X-ray photoelectron spectroscopy (XPS) [6,34] and infrared spectroscopy [32,40].

The present study examines NO adsorption on α -Al₂O₃-supported Ag catalysts as well as pure α -Al₂O₃ to probe the chemical state of the silver surface regarding the influence of pretreatment and promoters by utilizing in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), temperature-programmed desorption (TPD), and chemisorption measurements. Unlike dioxygen, NO adsorption can give gas-phase products such as N₂O that are detectable by FTIR as well as by TPD. Studies were conducted on unpromoted Ag/ α -Al₂O₃ as well as this catalyst promoted with either CsNO₃ (to study the effect of only Cs) or CsCl (to study the combined effect of both Cs and Cl).

2. Experimental

Details regarding the preparation of these supported catalysts, which contain approximately 15% Ag, have been given elsewhere [1]. An unpromoted catalyst, designated UNP-I, was prepared using α -Al₂O₃ (Norton Corp., SA 5562, 0.78 m²/g) and then calcined in a forced air oven at 493 K for 30 min. Four Cs-promoted catalysts were prepared with either a nominal 400 ppm Cs loading, designated CsN (409) and CsCl (412), or a nominal 1200 ppm Cs loading, designated CsN (1175) and CsCl (994), where the prefixes CsN and CsCl indicate either CsNO₃ or CsCl as the respective precursor and the number in parentheses indicates the analyzed Cs content in ppm. A sample of α -Al₂O₃ impregnated with 1000 ppm Cs using CsNO₃ precursor was also prepared and it is designated Cs (1000, no Ag). After impregnation, the promoted catalysts were calcined at 598 K in air for 30 min. It has been reported elsewhere that the average Ag particle size in UNP-I is somewhat smaller than that in the promoted catalysts, so experiments were also carried out on another unpromoted Ag/ α -Al₂O₃ catalyst (UNP-II) which was calcined at 598 K for 30 min, as were the promoted catalysts, to compare a more similar Ag crystallite size [41]. Properties of these six catalysts are tabulated in Table 1. Experiments were also performed with pure α -Al₂O₃.

Four different pretreatments using two sets of temperature were applied and the procedures are given below, where LT refers to the lower set of temperatures and HT refers to the higher set of temperatures shown in parentheses. After a specified pretreatment, these catalysts were characterized by NO and O₂ chemisorption, DRIFTS, TPD, and X-ray diffraction (XRD).

Table 1
Composition and Ag crystallite size of Ag/ α -Al₂O₃ catalysts

Catalyst	Silver ^a (%)	Cesium ^b (ppm)	Chlorine ^c (ppm)	<i>d</i> ^d (nm)
UNP-I	15.1	0	0	–
UNP-II	14.9	0	0	275
CsN (409)	15.5	409	0	283
CsCl (412)	14.4	412	130	247
CsN (1174)	10.8	1174	0	354
CsCl (994)	13.1	994	310	–

^a Analyzed by ICP-OES.

^b Analyzed by AAS.

^c Nominal content based on cesium content.

^d Particle size calculated based on SEM analysis.

I LT (HT) (reduced Ag surfaces)

1. Calcine 2 h at 523 (773) K in 20% O₂ at a total flow of 50 sccm;
2. Reduce 1 h at 473 (673) K in 20% H₂ at a total flow of 50 sccm;
3. Purge at 473 (673) K for 30 min under flowing He;
4. Cool to adsorption temperature.

After the pretreatment, 4% NO in He (or a mixture of 3% NO and 30% O₂ in He) for 30 min at a total flow of 20 sccm was introduced.

II LT (HT) (O-covered Ag surfaces)

1. After applying I-LT (HT), introduce 10% O₂ for 30 min at 443 K at a total flow of 20 sccm;
2. Purge at 443 K for 30 min under He flow;
3. Cool to adsorption temperature.

After this pretreatment, 4% NO in He (20 sccm total flow) for 30 min was introduced.

NO and O₂ chemisorption measurements were performed in a glass gas adsorption system capable of a vacuum of $< 1 \times 10^{-5}$ Torr in the adsorption cell [42]. The system was equipped with an Edwards Model EO2K oil diffusion pump backed by a Precision mechanical pump, and the vacuum was monitored by a Granville-Phillips Model 260 gauge controller. Isotherm measurements were obtained using a Mensor DPG II Model 15000 pressure transducer with 0.01% full-scale accuracy.

Ultrahigh purity (UHP) grade He and H₂ (99.999%, MG Ind.) were further purified by passing them through indicating Oxytraps (Alltech Assoc.). All gases including O₂ (99.999%, MG Ind.) were passed through molecular sieve traps, and NO (99%, MG Ind.) was used after passing it through Ascarite and CaSO₄ traps to remove CO₂ and water, respectively. ¹⁵NO (Cambridge Isotope Laboratories, 98%), which was introduced under static conditions, was used without further purification. Precise gas flow rates were maintained using mass flow controllers (Tylan Corp., Model FC-260). All DRIFT spectra were obtained at 300 K. Details

of the diffuse reflectance FTIR system used in the present study and the standard procedures employed to record spectra have been described in detail elsewhere [1]. After loading the sample into the DRIFTS reactor cell, the catalyst was purged overnight under a He flow. It was then subjected to an in situ pretreatment and cooled to 300 K to obtain the first interferogram which was used as the background reference for the subsequent spectra for that sample. Following this, 4% NO (or a mixture of 3% NO and 30% O₂) was introduced at 300 K for 30 min at 20 cm³/min, at which time a second interferogram was collected and, for some samples, additional interferograms were also recorded during this 30-min exposure to NO. Then the sample was purged with He for 30 min and another interferogram was taken at that temperature (third spectrum). The gases were fed under atmospheric pressure in all pretreatments and experiments. When ¹⁵N₂O was used, 30 Torr was admitted to the cell under nonflow conditions for 30 min. To determine the thermal stability of adsorbed species, the sample in the cell was heated to a certain temperature and then cooled to 300 K and a fourth interferogram was then collected. All spectra are reported as absorbance because the absorbance and Kubelka–Munk spectra were typically similar, but the K-M function does not display negative bands.

The temperature-programmed desorption experiments were performed at 1 atm using a small fixed bed of sample (100 mg, unless otherwise stated) placed in a 4 mm i.d. quartz tube that was 30 cm long. A mixture of 4% NO in He (MG Ind.) was used after passing through Ascarite and CaSO₄ traps to remove CO₂ and water, respectively. After applying the I-HT pretreatment, either a mixture of 3% NO (as 4% NO in He, MG Ind.) and 30% O₂ (UHP, MG Ind.) in He or 10% O₂ (UHP, MG Ind.) in He was introduced for 30 min followed by a 30-min purge. After that, TPD spectra were obtained by heating the sample from room temperature to 973 K at a rate of 50 K/min under a flow of 30 sccm He. A small portion of the effluent gas was routed via a needle valve to a leak valve and continuously monitored by an on-line, computer-controlled UTI quadrupole mass spectrometer for analysis.

XRD measurements were made using a Philips X'Pert MPD X-ray diffractometer with Cu-K_α radiation which was operated at 40 kV, 20 mA, and 0.2°/min with a 2° slit width.

3. Results

3.1. Chemisorption of O₂ and NO on Ag catalysts

Each sample was subjected to a I-HT pretreatment and then cooled to 443 K, at which temperature a monolayer coverage of oxygen is achieved [2–4], and O₂ uptakes were measured. NO chemisorption at 300 K was studied on Ag surfaces reduced at 673 K, and NO adsorption at 300 K on O-covered Ag surfaces was examined following either a II-HT pretreatment or an O₂ chemisorption measurement at

Table 2
Adsorption of O₂ at 443 K and NO at 300 K on Ag catalysts and α-Al₂O₃

Catalyst	Pretreatment	Gas uptakes (μmol/g _{cat})		
		O ₂ ^a	NO	NO _{(ad)}/O_(ad)}
UNP-I	I-HT	3.4 (1.0)	7.1	1.0
	II-HT	–	4.5	0.62
UNP-II	I-HT	2.8 (0.93)	5.5	0.98
	II-HT	–	2.6	0.46
CsN (409)	I-HT	2.5	6.6	1.32
	II-HT	–	3.6	0.72
CsCl (412)	I-HT	2.0	4.5	1.1
	II-HT	–	2.0	0.50
CsN (1175)	I-HT	2.0	8.1	2.0
	II-HT	–	2.7	0.67
CsCl (994)	I-HT	2.2	3.7	0.84
	II-HT	–	1.8	0.41
Ag powder	I-HT	0.82	1.0	0.61
	II-HT	–	0.65	0.40
α-Al ₂ O ₃	I-HT	0	0.28	–

^a O₂ adsorption at 300 K in parentheses.

443 K. The O₂ and NO uptakes are listed in Table 2, and the corresponding adsorption isotherms are provided elsewhere [43]. Oxygen uptakes after a low-temperature (LT) pretreatment involving reduction at 473 K have been discussed elsewhere in detail [41]. With the unpromoted catalysts, the irreversible “O” uptake was higher on UNP-I than on UNP-II (6.8 μmol/g_{cat} versus 5.6 μmol/g_{cat}, respectively). The irreversible uptake of 5.0 μmol O/g_{cat} on CsN (409) was slightly lower than on its unpromoted counterpart, UNP-II, while lower oxygen uptakes of 4.0, 4.0, and 4.4 μmol O/g_{cat}, were measured on CsCl (412), CsN (1175), and CsCl (994), respectively. The O uptake on Ag powder was 1.64 μmol/g, and no irreversible oxygen adsorption occurred on α-Al₂O₃ alone.

To examine the effect of the support, NO chemisorption at 300 K was first measured on pure α-Al₂O₃ after a I-HT pretreatment and the uptake was 0.28 μmol/g, which indicates that no significant nitric oxide adsorption occurred. The NO uptake was 1.0 μmol/g on reduced Ag powder, 7.1 μmol/g_{cat} on UNP-I, and 5.5 μmol/g_{cat} on UNP-II. The irreversible NO uptakes of 8.1 and 6.6 μmol/g_{cat} on CsN (1175) and CsN (409), respectively, are higher than that on their unpromoted counterpart, UNP-II, whereas the NO uptakes of 3.7 and 4.5 μmol/g_{cat} for CsCl (994) and CsCl (412), respectively, were lower than those on the UNP and CsN catalysts. The ratio of the NO uptake on the reduced Ag surface at 300 K to the O uptake at 443 K was found to be close to or slightly higher than unity for all catalysts except the two CsN catalysts, and this is discussed later. After a II-HT pretreatment, NO uptakes on the O-covered unpromoted catalysts were 4.2 and 2.6 μmol/g_{cat} for UNP-I and UNP-II, respectively, while they were 2.7 and 3.6 μmol/NO/g_{cat} on CsN (1175) and CsN (409), respectively. The NO uptake was 1.8 μmol/g_{cat} on O-covered CsCl (994), 2.0 μmol/g_{cat}

on O-covered CsCl (412), and 0.65 $\mu\text{mol/g}_{\text{cat}}$ on O-covered Ag powder.

3.2. DRIFTS results

Gas-phase spectra for ^{14}NO and ^{15}NO have been provided elsewhere which show bands at 1875 (1841) and 2224 (2154) cm^{-1} due to the NO stretching vibration of ^{14}NO (^{15}NO) and the $\text{N}\equiv\text{N}$ stretching of $^{14}\text{N}_2\text{O}$ ($^{15}\text{N}_2\text{O}$), respectively [43], because the latter gases were present as an impurity in the gas cylinders. These spectra were subtracted from the corresponding spectra taken after exposure of any sample to ^{14}NO (^{15}NO); therefore, any significant N_2O formation during NO adsorption could be differentiated from the impurity.

DRIFT spectra after exposure of $\alpha\text{-Al}_2\text{O}_3$ to NO at 300 K following a I-HT pretreatment are given elsewhere and demonstrate no detectable NO adsorption [43]. In addition to some OH, Al–O, and gas-phase N_2O stretching bands, a weak band at 1640 cm^{-1} was observed which is attributed to a bending mode of chemisorbed water because, as stated later in this section, this band position did not shift after ^{15}NO adsorption on supported Ag catalysts.

Fig. 1 illustrates DRIFT spectra of NO adsorbed on UNP-II after a I-LT pretreatment. After exposure of this sample to NO for 1 min, a band at 2222 cm^{-1} due to the $\text{N}\equiv\text{N}$ stretching mode of N_2O was observed after subtracting the gas-phase NO spectrum, and after a 30-min exposure to NO, a band appeared at 1640 cm^{-1} ; however, the intensity of these bands is low and it is difficult to distinguish them from the impurity level as explained under Discussion. The time dependency of the spectra was also investigated with this sample and spectra were taken after 30, 60, and 100 min of exposure to NO. These spectra exhibited the same IR features, as shown by the third and fourth spectra in Fig. 1, and the intensity of the band at 1232 cm^{-1} was greater after a 100-min NO exposure compared to that of the 1213 cm^{-1}

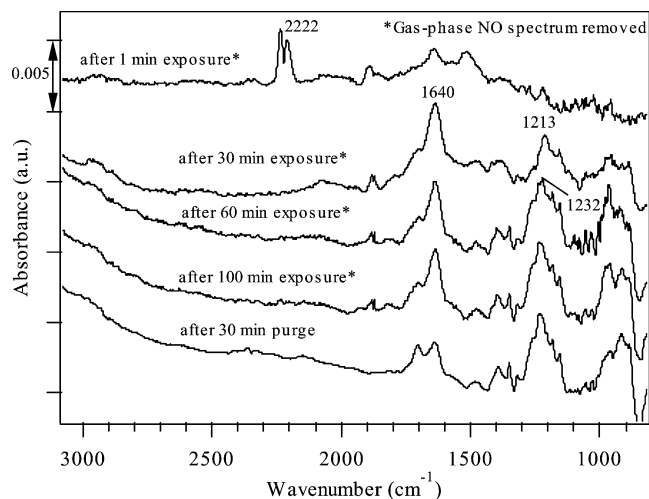


Fig. 1. DRIFT spectra of NO adsorbed on UNP-II at 300 K after a I-LT pretreatment.

band observed after a 30-min exposure. NO adsorption on a UNP-I catalyst after a I-LT pretreatment gave no significant IR features [43].

After a HT pretreatment, bands were similar for either UNP-I or UNP-II [43]; therefore, only results with UNP-I are presented here. Fig. 2a shows DRIFT spectra after NO adsorption following reduction at 673 K. As with reduced UNP-II, gas-phase N_2O was formed after the introduction of NO for 1 min, and bands at 1640 and 1161 cm^{-1} were observed after 30 min. To better identify these adsorbed species, an isotope study was conducted and ^{15}NO was adsorbed on UNP-I after the same pretreatment but continuous flow was not used. The spectra in Fig. 2b show bands at 2154 and 1265 cm^{-1} which are due to $^{15}\text{N}^{15}\text{N}$ and ^{15}NO stretching modes, respectively, of gas-phase $^{15}\text{N}_2\text{O}$. The position of the 1165 cm^{-1} band was the same after either ^{14}NO or ^{15}NO adsorption, which indicates that this band does not involve a “N” atom. Unlike ^{14}NO , ^{15}NO was not introduced continuously; thus, the intensity of gas-phase $^{15}\text{N}_2\text{O}$ increased as

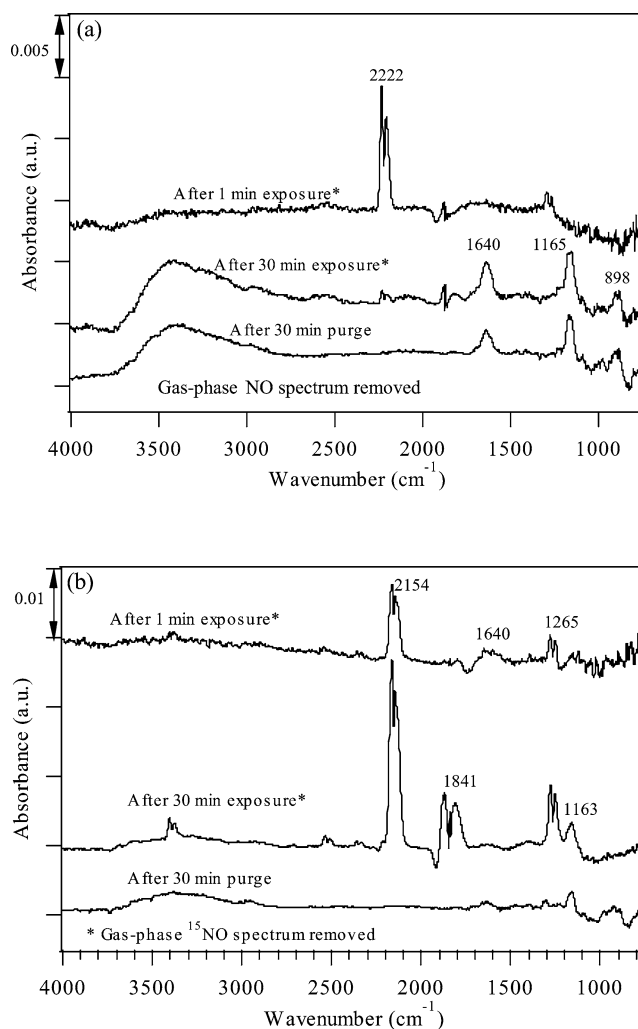


Fig. 2. DRIFT spectra of (a) NO and (b) ^{15}NO adsorbed on UNP-I at 300 K after a I-HT pretreatment.

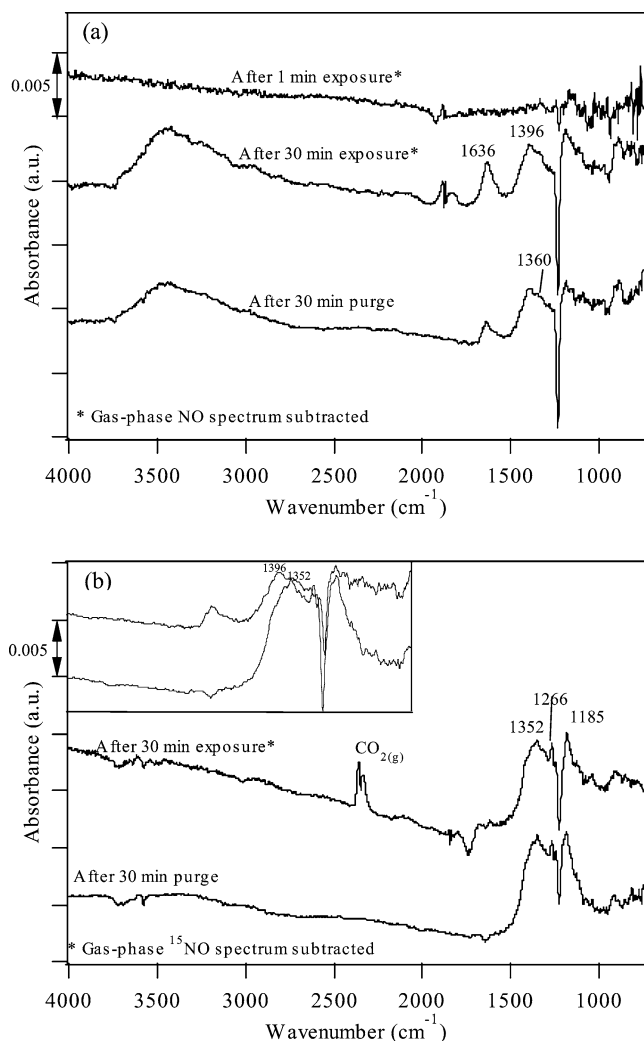


Fig. 3. (a) DRIFT spectra of ^{14}NO adsorbed on UNP-I at 300 K after a II-HT pretreatment; (b) DRIFT spectra of ^{15}NO adsorbed on UNP-I at 300 K after a II-HT pretreatment; inset shows comparison of spectra taken after a 30-min purge, i.e., ^{14}NO (third spectrum in (a)) and ^{15}NO (second spectrum in (b)).

exposure time increased, indicating that continuous formation of nitrous oxide occurs during exposure to NO.

Figs. 3a and 3b depict spectra obtained after either ^{14}NO or ^{15}NO adsorption on UNP-I after a II-HT pretreatment. In contrast to the reduced catalyst, gas-phase N_2O was not observed over the O-covered sample. The band near 1396 cm^{-1} after ^{14}NO adsorption (Fig. 3a) was red-shifted to 1352 cm^{-1} after ^{15}NO adsorption (Fig. 3b), which implies that this band is due to a species containing nitrogen.

A comparison between NO and O_2 adsorption on Cs-promoted $\alpha\text{-Al}_2\text{O}_3$ after a I-LT pretreatment has been shown elsewhere [43]. Except for some gas-phase N_2O formation during exposure to NO, the weak IR features were similar after exposure to either NO or O_2 . Considering possible assignment of the band positions, it is proposed that the bands at 1655 , 1390 , and 1362 cm^{-1} were due to a CO_2 impurity in both the O_2 and NO cylinders, as noted later.

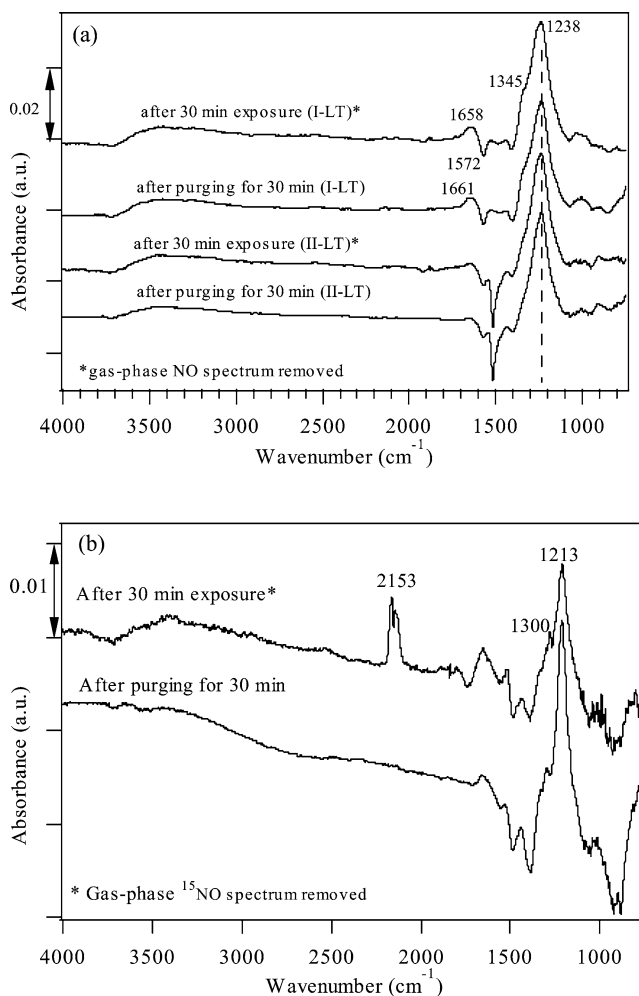


Fig. 4. (a) DRIFT spectra of ^{14}NO adsorbed at 300 K on CsN (1175) after either a I-LT or a II-LT pretreatment. (b) DRIFT spectra of ^{15}NO adsorbed at 300 K on CsN (1175) after a I-LT pretreatment.

Fig. 4a illustrates DRIFT spectra taken after NO adsorption on CsN (1175) following either a I-LT or a II-LT pretreatment. As with the Cs/ $\alpha\text{-Al}_2\text{O}_3$ sample, a band near 1660 cm^{-1} was again observed, which suggests that it is a surface species due to Cs. In addition, a dominant band appeared at 1238 cm^{-1} with a shoulder around 1345 cm^{-1} and weak “negative” bands at 1573 and 1407 cm^{-1} occurred for the reduced sample while a different, sharper negative peak occurred with the O-covered sample. After a 30-min exposure of CsN (1175) to ^{15}NO following a I-LT pretreatment, gas-phase $^{15}\text{N}_2\text{O}$ and bands at 1213 and 1300 cm^{-1} were observed as shown in Fig. 4b. Their red shift compared to their counterparts at 1238 and 1345 cm^{-1} indicated that both are due to a species containing “N.”

Figs. 5a and 5b show NO adsorption on CsN (1175) after either a I-HT or a II-HT pretreatment. After exposure to 30 Torr NO for 1 min, gas-phase N_2O was present to give a band at 2223 cm^{-1} and a broad band at 1510 cm^{-1} appeared as soon as NO was introduced. As exposure time increased, this latter peak shifted to 1520 cm^{-1} and its intensity in-

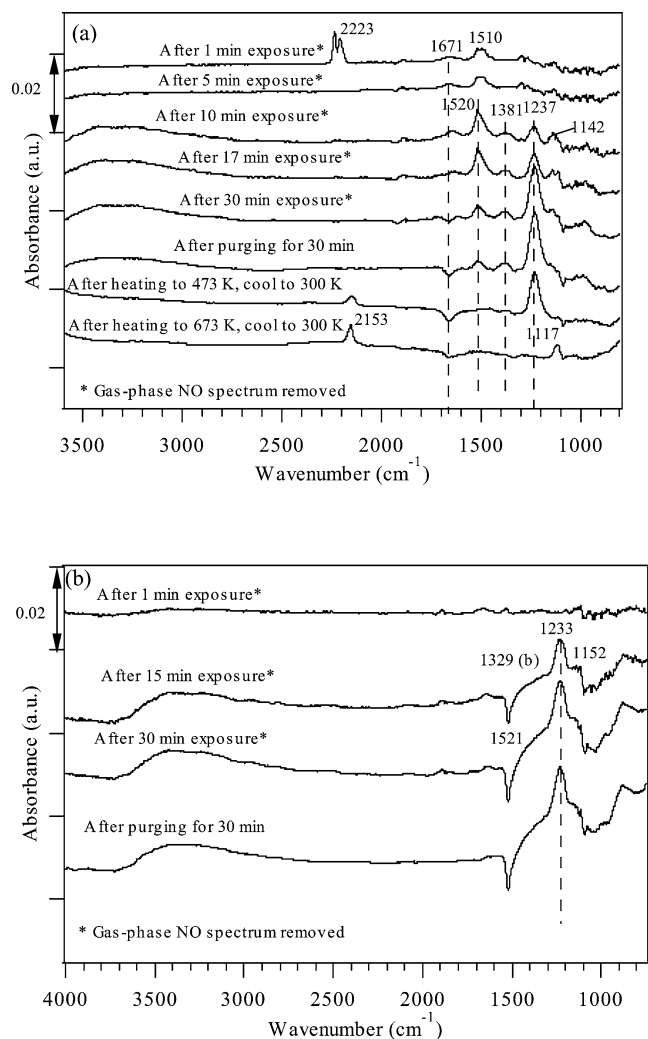


Fig. 5. DRIFT spectra of NO adsorbed on CsN (1175) at 300 K: (a) after a I-HT pretreatment; (b) after a II-HT pretreatment.

creased; however, after exposures larger than 17 min, the intensity of this band decreased simultaneously as the band intensity at 1237 cm^{-1} increased. In addition, a weak band at 1142 cm^{-1} was observed after a 10-min NO exposure which remained as a shoulder after a 30-min purge. Bands near 1670 and 1380 cm^{-1} were observed as with adsorption of NO on the Cs/ $\alpha\text{-Al}_2\text{O}_3$ sample. After heating this sample to 473 K and cooling it to 300 K , the bands at 1670 , 1520 , and 1380 cm^{-1} disappeared and a band at 2153 cm^{-1} developed. The intensity of the 1237 cm^{-1} band decreased and, after heating to 673 K , it completely disappeared, as shown in the eighth spectrum in Fig. 5a. After this last heating cycle, the intensity of the band at 2153 cm^{-1} increased and a band at 1117 cm^{-1} appeared.

To help identify these surface species, experiments were conducted with ^{15}NO , and Fig. 6 illustrates the spectra taken after ^{15}NO adsorption on CsN (1175) following reduction at 673 K . After ^{15}NO adsorption, gas-phase $^{15}\text{N}_2\text{O}$ was present to give bands at 2154 and 1265 cm^{-1} due to NN and NO

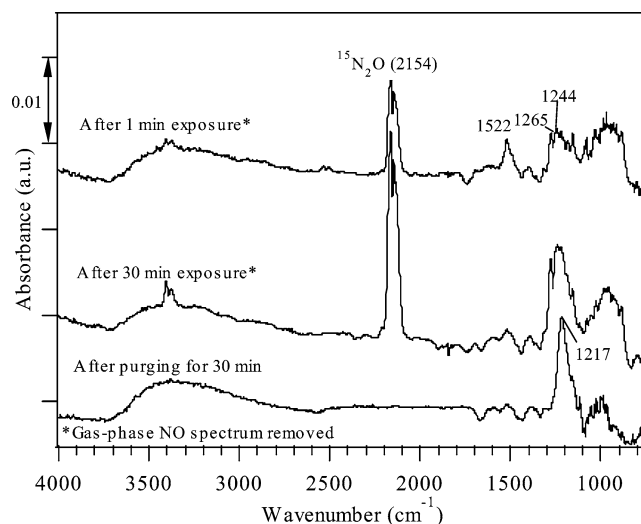


Fig. 6. DRIFT spectra of ^{15}NO adsorbed on CsN (1175) at 300 K after a I-HT pretreatment.

stretching modes, respectively. The band at 1217 cm^{-1} is the counterpart of the 1237 cm^{-1} band, suggesting that this surface species contains N. In addition, a band at 1522 cm^{-1} , similar to that at 1520 cm^{-1} after ^{14}NO adsorption, existed, and the absence of a red shift suggests that this is not an N_xO_y species, as discussed later.

NO was adsorbed on the CsCl (994) catalyst to examine the combined effect of Cs and Cl. As with all other samples, after a 1-min exposure to NO following reduction at 473 K , gas-phase N_2O was present, as shown in Fig. 7. The band at 1238 cm^{-1} showed a time-dependent increase in intensity after ^{14}NO adsorption and it was red-shifted after ^{15}NO adsorption to 1211 cm^{-1} , while bands between 1616 and 1626 cm^{-1} and 1352 and 1381 cm^{-1} occurred after either ^{14}NO or ^{15}NO adsorption. After a 30-min purge, the band intensity at 1238 (or 1211) cm^{-1} remained the same. After heating the sample to 473 K and cooling to 300 K to take a spectrum, a band near 1500 cm^{-1} band was formed, as shown in Figs. 7a and 7b. After a I-LT, a II-LT, or a I-HT pretreatment, absorption features were similar to those in Fig. 7 [43], so the latter two sets of spectra are not presented.

Figs. 8a and 8b display DRIFT spectra taken after coadsorption of NO and O_2 (3 and 30%) on supported Ag catalysts, $\alpha\text{-Al}_2\text{O}_3$, Cs/ $\alpha\text{-Al}_2\text{O}_3$, and promoted Ag/ $\alpha\text{-Al}_2\text{O}_3$ after either a 30-min exposure or a 30-min purge following the NO + O_2 exposure. When a mixture of NO and O_2 was introduced, gas-phase NO_2 (1616 cm^{-1}) and N_2O_4 (1756 and 1271 cm^{-1}) were formed. After purging, all gas-phase NO_x compounds were removed while the bands between 1355 and 1393 , 1326 and 1361 , and 1433 and 1474 cm^{-1} retained the same intensity for all samples, and residual peaks at 1757 and 2346 cm^{-1} remained with the supported Ag catalysts (Fig. 8b). Bands at 1584 , 1414 , 1355 , and 1322 cm^{-1} were generated on alumina, while a dominant band appeared at 1379 cm^{-1} with Cs/ $\alpha\text{-Al}_2\text{O}_3$.

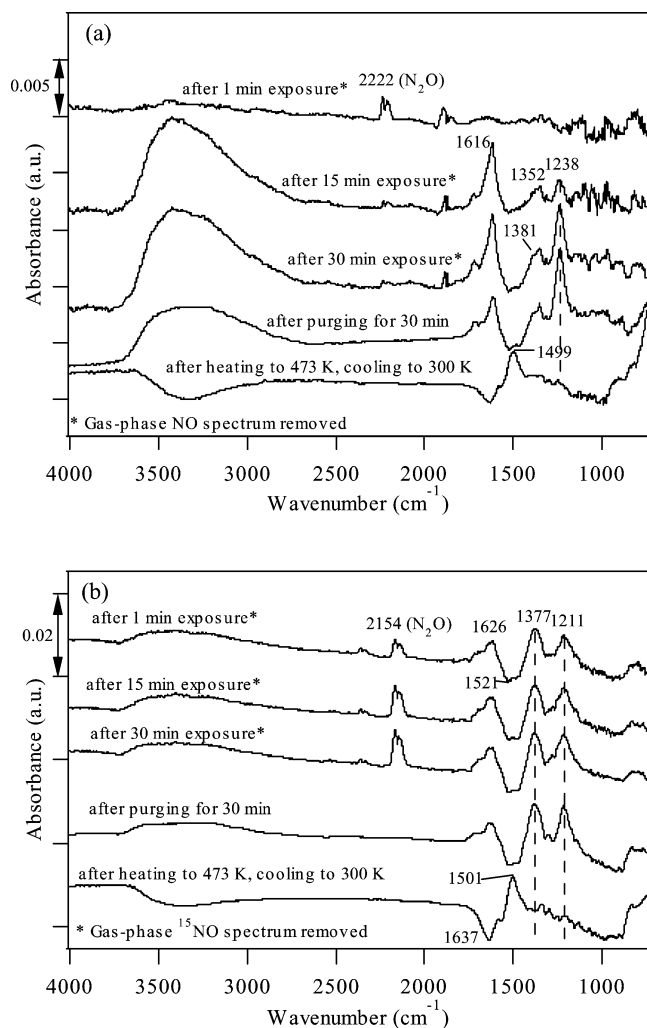


Fig. 7. DRIFT spectra of (a) ^{14}NO and (b) ^{15}NO adsorbed on CsCl (994) at 300 K after a I-LT pretreatment.

3.3. Mass spectroscopy and TPD

The effluent gas from the TPD cell was analyzed by mass spectroscopy during NO adsorption at 300 K. Fig. 9a clearly shows that the introduction of NO to a reduced UNP-I catalyst initially produced a significant amount of N_2O , and similar behavior occurred with reduced samples of the promoted Ag catalysts [43]. In contrast, with O-covered Ag surfaces, the introduction of NO at 300 K did not produce any N_2O formation, as seen in Fig. 9b, and similar results were obtained with the promoted Ag catalysts and alumina after a II-HT pretreatment [43]. During a TPD run after exposure of a catalyst to a NO/ O_2 mixture following a I-HT pretreatment, one desorption maximum was observed for NO, O_2 , N_2O , and N_2 around 620–660 K with all the Ag catalysts, and Fig. 10a shows TPD results with UNP-I as a representative run. On pure $\alpha\text{-Al}_2\text{O}_3$ after a I-HT pretreatment, TPD was performed after the introduction of a NO/ O_2 mixture, as shown in Fig. 10b. No O_2 desorption peak occurred, while three weak desorption maxima for NO were observed at 465,

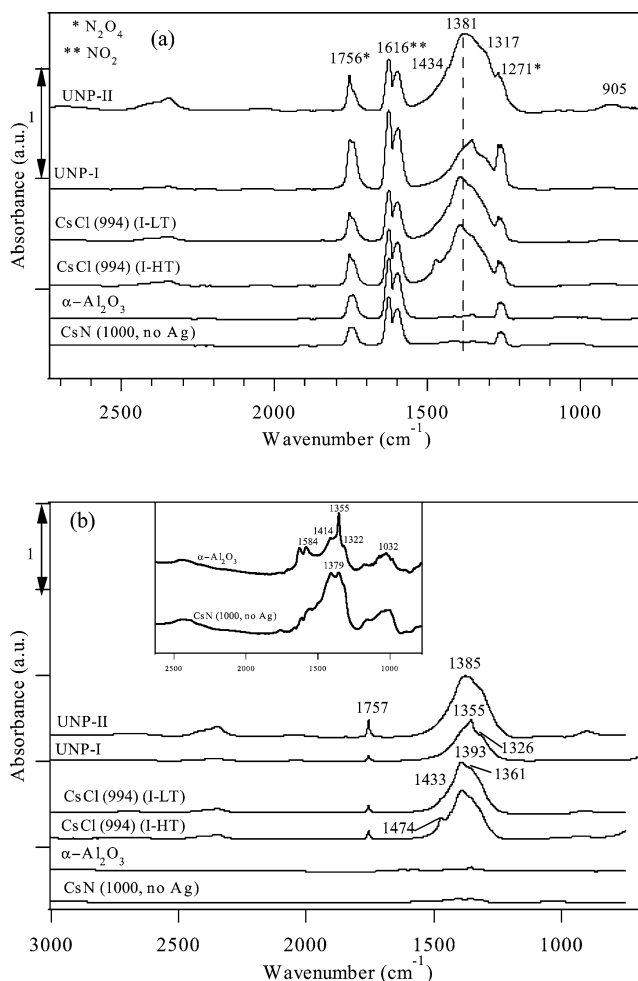


Fig. 8. DRIFT spectra of NO adsorbed in the presence of O_2 (23:230 Torr) at 300 K after a I-HT pretreatment, unless otherwise stated: (a) after 30-min exposure; (b) after a 30-min purge; inset shows expanded scale for spectra of alumina and CsN (1000, no Ag) in the 1000–2500 cm^{-1} spectral region.

680, and 750 K. O_2 TPD was also conducted to probe the effect of Cs and to compare the adsorption behavior of oxygen in the presence and absence of NO. Fig. 11 displays TPD results for UNP-II and CsN (1175) after exposure to 76 Torr O_2 at 443 K following a I-HT pretreatment, and respective O_2 desorption peaks were observed at 560 and 530 K, indicating weaker oxygen adsorption on Cs-promoted Ag.

4. Discussion

Previous NO adsorption studies have been conducted with Ag single crystals and Ag films, mostly at subambient temperatures although a few studies have utilized ambient temperature. Lambert and co-workers conducted one of the earliest surface science studies on NO adsorption on Ag (111) and Ag (110) at 300 K using LEED, AES, and TDS [20–22], and NO adsorption was found to be molecular and reversible with a sticking probability of 0.1, which is very high in comparison with the sticking probability of O_2

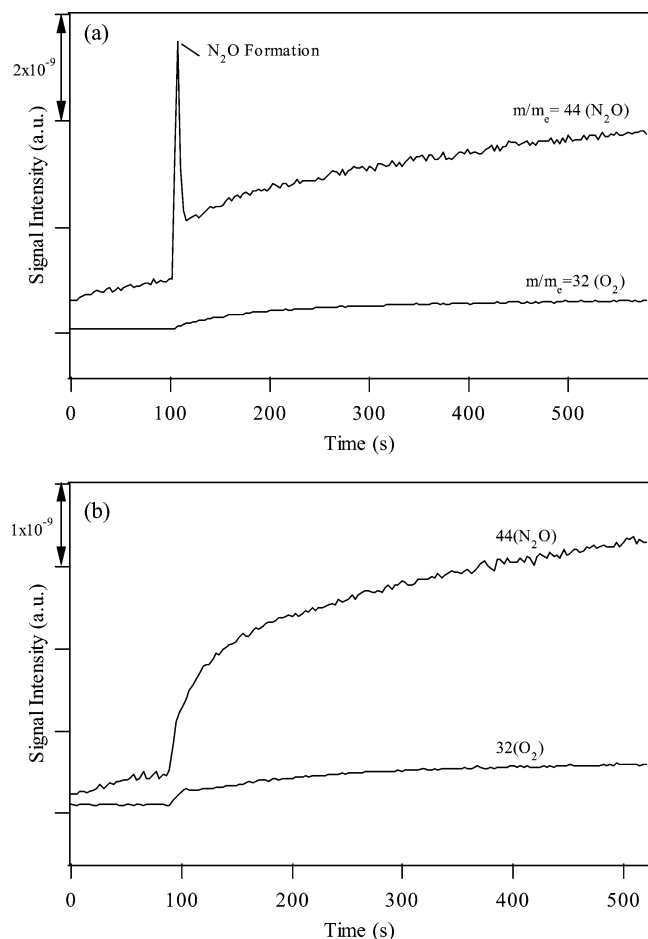


Fig. 9. (a) N_2O formation during initial NO adsorption on UNP-I at 300 K after a I-HT pretreatment; (b) during initial NO adsorption on UNP-I at 300 K after a II-HT pretreatment.

($\sim 10^{-4}$ on Ag (110) and 10^{-6} on Ag (111)) [44]. The NO coverage was low and gave a comparatively high desorption activation energy of 24.7 kcal/mol. In contrast to these results, Edamoto et al. reported that no adsorbed species existed at 300 K [26]. Similarly, Bao et al. examined the coadsorption of NO and O_2 on a Ag (110) surface and found that when only NO was introduced below 375 K, no evidence for NO adsorption was obtained using Raman spectroscopy [37]. XPS and UPS monitored a small amount of bulk oxygen, but no signals relevant to surface oxygen and nitrogen were detected. Hadjiivanov studied NO_x adsorption on Ag-ZSM-5 at 300 K using IR spectroscopy and, after introduction of 10 Torr NO, a weak band at 1634 cm^{-1} occurred which was stable toward evacuation and was assigned to bridged surface nitrate species [19]. The formation of NO_3^- species requires adsorbed O atoms; thus, this study implied NO dissociation on Ag because this was the only O source. In most of the studies conducted at subambient temperatures, the formation of NO_2 and NO_3 species was not observed but N_2O and the $(\text{NO})_2$ dimer were detected [6,27,32]. However, these different conclusions were reached based on different coverages, temperatures, and techniques. Bartollucci and

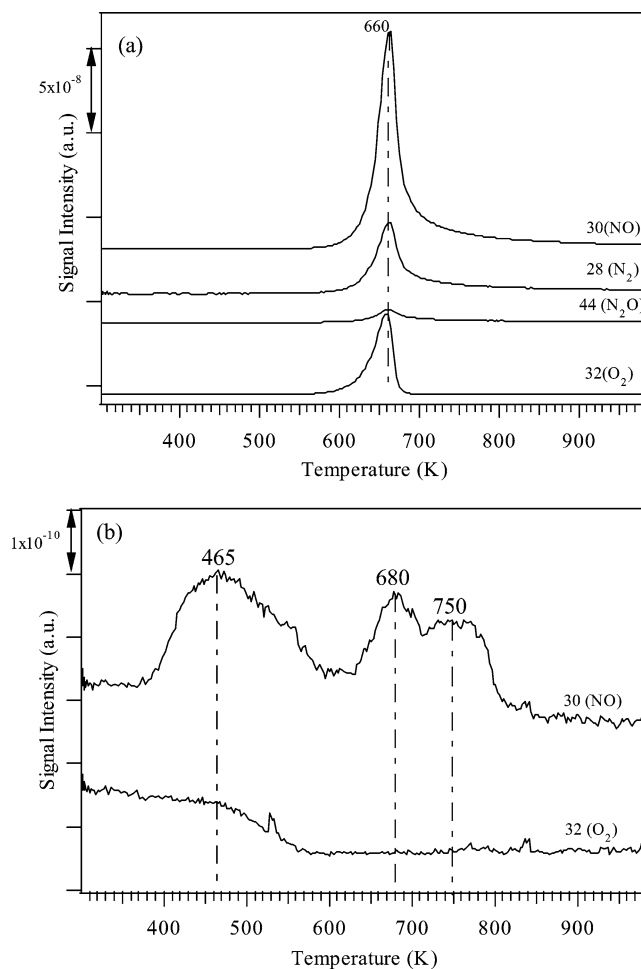


Fig. 10. TPD after NO adsorption in the presence of O_2 (a mixture of 3% NO and 30% O_2) at 300 K on (a) UNP-I; (b) $\alpha\text{-Al}_2\text{O}_3$.

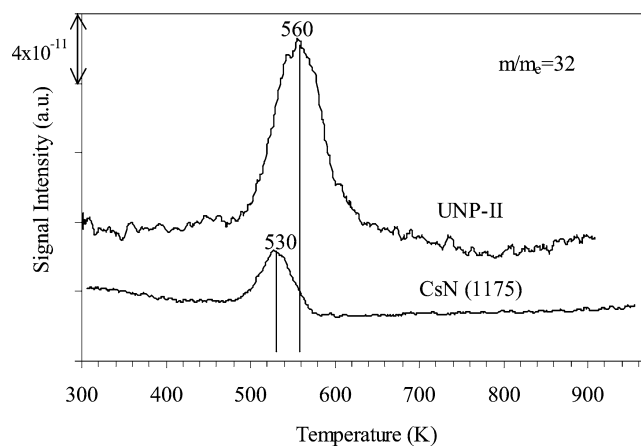


Fig. 11. TPD after O_2 adsorption at 443 K on unpromoted Ag/ $\alpha\text{-Al}_2\text{O}_3$ and Cs-promoted Ag/ $\alpha\text{-Al}_2\text{O}_3$ following reduction at 673 K.

Otto used SERS to investigate the transformation of NO and NO_2 on silver films at 30–40 K, and they found that after exposure to 10 L NO, strong signals were detected originating from NO_2^- , N_2O , and atomic oxygen [30]. Although this work was performed at subambient temperatures similar to

the previous studies, Bartolucci and Otto did not observe any signal due to NO, which they interpreted to mean that NO adsorption on Ag is structure sensitive.

4.1. Band assignments

NO chemisorption can be divided into reactive and non-reactive adsorption. During nonreactive adsorption, surface mononitrosyl and dinitrosyl complexes are formed [45]. DRIFT spectra have not detected the formation of nitrosyl complexes, $\nu(\text{NO})$, on Ag, which have wavenumbers ranging from 1900 to 1500 cm^{-1} . This is in accordance with the study by Hadjiivanov which reported that NO adsorption on Ag-ZSM-5 did not lead to formation of nitrosyl complexes due to the weak electrophilicity of the univalent Ag^+ ions and the absence of any π back-donation of electrons [19].

Most of the studies of NO on Ag have reported the formation of an N_2O or NO dimer on the surface at subambient temperatures. In our current study, gas-phase N_2O was observed by DRIFTS and mass spectroscopy during NO adsorption at 300 K on all the reduced Ag catalysts, which necessitates NO dissociation on metallic silver. This result agrees with that of Brown et al., who reported that N_2O adsorbed on silver surfaces at low temperatures begins to desorb at 120 K [32]. An isotopic study using ^{15}NO was conducted with unpromoted and Cs-promoted samples by introducing ^{15}NO to the reduced sample under static conditions [43]. The intensity of the band due to gas-phase $^{15}\text{N}_2\text{O}$ increased as the exposure time increased, which indicates that NO continued to oxidize metallic silver atoms during the 30-min exposure period. IR bands due to gas-phase N_2O were also detected after NO adsorption on HT-pretreated alumina, although with the same sample no N_2O was detected using mass spectroscopy. The NO uptake on $\alpha\text{-Al}_2\text{O}_3$ was only 0.28 $\mu\text{mol/g}$, which implies that NO may dissociate on alumina but to a much lesser extent. With all the supported Ag samples, a band between 1620 and 1640 cm^{-1} was observed. Although many NO_x species (NO_2 , nitrites, nitrates) absorb in this region, our studies of NO adsorption on alumina and ^{15}NO adsorption on supported Ag catalysts have demonstrated that this band is due to a bending mode of trace amounts of water chemisorbed on alumina [1].

With Cs-promoted samples, bands were observed between 1500 and 1480 cm^{-1} with either negative or positive intensities. Negative bands appeared in this spectral region with LT- and II-HT-pretreated samples, and this suggests that certain species on the surface were removed during NO exposure. With a I-HT-pretreated CsN (1175) catalyst, a band developed at 1520 cm^{-1} during the initial adsorption of NO but its intensity decreased as exposure time increased. Similar behavior was observed for a 1472 cm^{-1} band with I-HT-pretreated CsCl (994). Fig. 12 provides a comparison between CO and NO adsorption on CsN (1175) and shows that bands in the 1470–1530 cm^{-1} spectral region were evident after adsorption of either gas, which suggests that these bands may be due to carbonate compounds. Similar features

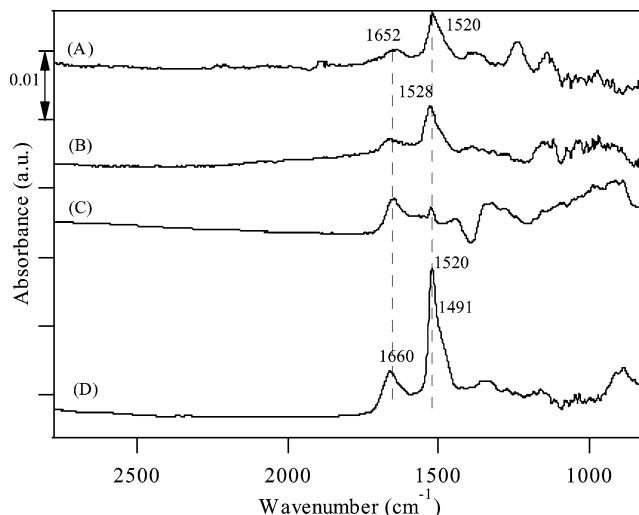
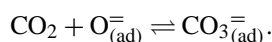


Fig. 12. Comparison of DRIFT spectra taken for CsN (1175) at 300 K: (A) after a 10-min exposure to 30 Torr NO after a I-HT pretreatment; (B) after a 30-min exposure to 76 Torr O_2 after a I-HT pretreatment; (C) after a 30-min CO adsorption (76 Torr) following a II-LT pretreatment; (D) after a 30-min CO adsorption (76 Torr) following a II-HT pretreatment (all spectra were taken after a 30-min purge).

were present after O_2 adsorption ([43] and spectrum B in Fig. 12). Although it might be considered that these bands were due to molecularly adsorbed oxygen, as reported earlier for metal oxides [46–49], the observation of similar bands after CO adsorption on O-covered Ag catalysts provides a strong argument that these IR features are due instead to carbonate formation. This proposal implies that both O_2 and NO cylinders have a CO_2 impurity. Because the Ag surface areas of the supported catalysts are small, even a low concentration of impurities could have a significant effect, and our use of Ascarite to remove CO_2 may not be completely efficient. After the initial exposure of CsN (1175) to NO, a band at 1520 cm^{-1} occurred, which was assigned to carbonate formation on AgCs_xO_y sites [1]. As exposure time increased, NO adsorption led to an exchange reaction with CO_3^{2-} groups because NO competes for basic oxygen anions on the surface and can displace CO_2 as it is a stronger Lewis acid, as shown in Fig. 5a. Zemlyanov and Schlögl studied the interaction of the Ag (111) surface with NO, O_2 , and an NO/ O_2 mixture at 330 K using XPS, and they reported that two peaks were observed which are characteristic of carbonates and likely reflect that the oxygen atoms associated with these carbonate species possess different charges [38]. In fact, the carbonate species is easily produced by the following reaction:



This implies that in the current study CO_2 (a Lewis acid) desorbed from the surface and left basic oxygen anions on the surface; therefore, gas-phase CO_2 should be present during loss of surface carbonate groups. However, CO_2 formation was not always detected in these experiments, which is presumably due to the flow of the He carrier stream which

Table 3
NO₂⁻ band assignments

Compound		Asymmetric N–O ₂ stretch ν_a (cm ⁻¹)	Symmetric N–O ₂ stretch ν_s (cm ⁻¹)	NO ₂ deformation δ (cm ⁻¹)	Reference
Free NO ₂ ⁻		1250	1335	–	[49]
Nitro complex		1470–1370	1340–1320	–	[49]
		1335–1440	1350–1315	–	[59]
Nitrito complex		$\nu(\text{N=O})$	$\nu(\text{NO})$	–	[49]
		1485–1400	1110–1050	–	[59]
Chelating nitro		1450–1470	1050–1065	–	[59]
		1260–1390	1170–1210	840–860	[49]
Bridging nitrite		1220–1205		–	[45]
Inorganic compound		1343–1388	1222–1260	813–866	[52]
		1330	1240	810	[53]
		1284–1328	1176–1261	828–867	[54]
		1328–1375	1180–1318	810–832	[55]
		1337–1429	1114–1220	817–846	[56]

would continuously purge any desorbed CO₂. A displacement reaction is apparent, but it is not clear why the CO₂ impurity is preferably adsorbed on the surface during the initial NO exposure because NO is a stronger acid. These results have shown that the LT pretreatment at 473 K does not completely remove carbonate compounds which were presumably formed during exposure of the catalyst to CO₂ in the ambient air. Carbonate compounds were also formed after a II-LT or a II-HT pretreatment, which included exposure to O₂ at 443 K for 30 min and therefore to CO₂ as an impurity in the oxygen cylinder.

This displacement reaction gave rise to a band around 1238 cm⁻¹ for both Cs and CsCl-promoted catalysts, regardless of the pretreatment, which could be ascribed to NO₂⁻, NO₃⁻, NO⁻, or (NO)₂²⁻ species. The possible presence of NO⁻ species will first be discussed. When NO is adsorbed on a metal oxide such as Cr₂O₃ and MgO, the negatively charged nitrosyl ion, NO⁻, and the dimeric hypnitrite ion, (NO)₂²⁻, are also observed in addition to nitrite and nitrate species [50,51]. The formation of a bond between nitric oxide and any atom or group of atoms is accompanied by an increase of the electron density in the π^* orbitals of NO, which weakens the N–O bond, increases in the N–O distance, and leads to a shift in $\nu(\text{NO})$ to as low as 1040 cm⁻¹ [50]. However, when the sample was oxidized, NO⁻ species were not observed [50]. In our study, the same band was obtained after NO adsorption on either a clean Ag surface or an O-covered Ag surface; thus, the 1238 cm⁻¹ band cannot be assigned to NO⁻. In the same manner, (NO)₂²⁻ can be observed only on a reduced surface; hence, this band cannot be assigned to (NO)₂²⁻. A recent review of the identification of NO_x surface species by IR spectroscopy has pointed out the disagreement that exists in the assignment of IR bands to different NO_x⁻ species, and

Table 4
NO₃⁻ band assignments [Ref. from [49,57–61]]

Compound		Vibration	Band positions (cm ⁻¹)
Free nitrite ion NO ₂ ⁻		$\nu(\text{NO}_{2,\text{as}})$	1380
Bidentate nitrate		$\nu(\text{NO}_{2,\text{as}})$	1200–1310
		$\nu(\text{N=O})$	1500–1620
		$\nu(\text{NO}_{2,\text{s}})$	1003–1040
Unidentate nitrate		$\nu(\text{NO}_{2,\text{as}})$	1450–1570
		$\nu(\text{NO}_{2,\text{s}})$	1250–1330
		$\nu(\text{NO})$	970–1035
Bridging nitrate		$\nu(\text{NO}_{2,\text{as}})$	1170–1300
		$\nu(\text{NO}_{2,\text{s}})$	1000–1030
		$\nu(\text{NO})$	1590–1660
Inorganic compounds		$\nu(\text{NO}_{2,\text{as}})$	1470–1531
		$\nu(\text{NO}_{2,\text{s}})$	1253–1304
		$\nu(\text{NO})$	970–1055

some guidelines were provided for the identification of these surface species [45]. There have been many studies in the literature to differentiate among band positions assigned to NO₂⁻ and NO₃⁻ groups. The early studies between 1957 and 1970 were performed with inorganic complexes such as KNO₂, KNO₃, and NaNO₂ [52–59] and they showed that nitrite complexes and nitrate complexes gave similar bands. Tables 3 and 4 list assignments to NO₂⁻ and NO₃⁻ species based on inorganic compounds and metal oxides [45,49,52–61]. In the current study, nitrate species were observed between 1300 and 1475 cm⁻¹ after coadsorption of NO and O₂ on all supported Ag catalysts, as discussed later; therefore, the band at 1238 cm⁻¹ was not assigned to a nitrate compound. When the N–O bonds in the NO₂ group are equivalent, a single band around 1200–1220 cm⁻¹ is observed because both symmetric and antisymmetric stretching vi-

brations, $\nu(\text{NO}_2)$, have nearly the same frequency and are not resolved [49]; consequently, the 1238 cm^{-1} band may be assigned to $\nu(\text{NO}_2)$ of a chelating nitrito species. The experimental isotope shift with ^{15}NO was between 20 and 26 cm^{-1} for this band with I-HT-pretreated CsN (1175) and CsCl (994) samples. The chelating nitrito species preserve, in general, the C_{2v} symmetry [44]. Pinchas and Laulicht have reported that for harmonic, nonlinear, symmetrically labeled Y–X–Y molecules, the following relation holds [62],

$$\left(\frac{\nu_3^i}{\nu_3}\right)^2 = m_X m_Y (m_X^i + 2m_Y^i \sin^2 \alpha) / m_X^i m_Y^i (m_X + 2m_Y \sin^2 \alpha), \quad (1)$$

where ν_3 is the normal asymmetric stretching frequency of the Y–X–Y molecule, m_X and m_Y are the atomic weights of its X and Y atoms, α is half the YXY angle, and the superscript i denotes quantities belonging to the respective labeled molecule. Assuming that the NO_2^- oscillator is harmonic and the ONO angle is 134° [63], a wavenumber of 1211 cm^{-1} is calculated for ^{15}NO [43], which agrees well with the experimental values between 1217 and 1211 cm^{-1} .

A band between 1330 and 1396 cm^{-1} was observed with unpromoted Ag, Cs, and CsCl-promoted Ag catalysts, and the Cs/ Al_2O_3 sample. The bands at 1360 and 1390 cm^{-1} for the Cs/ Al_2O_3 sample may be due to cesium carbonate species because similar bands were observed after CO adsorption on this sample [1]. In addition, after ^{14}NO and ^{15}NO adsorption on CsCl (994), no change in position occurred for the 1381 cm^{-1} band, which implies that this band involves no N atoms and therefore may be due to a COO^- stretching mode of a carbonate compound. The band in this region with CsN (1175) after either a LT or a II-HT pretreatment may have contributions from both carbonate and nitrate species. After ^{15}NO adsorption on CsN (1175) following reduction at 473 K, the band at 1345 cm^{-1} shifted to 1300 cm^{-1} , which supports the idea that this band is due to NO_x species. A similar study was conducted with ^{15}NO and UNP-I, and after ^{15}NO adsorption on the O-covered catalyst, the band at 1396 cm^{-1} red-shifted to 1352 cm^{-1} . Coadsorption of NO and O_2 was also useful in assigning the bands observed in this spectral region. The introduction of a mixture of NO and O_2 created a band between 1355 and 1385 cm^{-1} with all samples, which was assigned to nitrate species, as discussed later. Therefore, we conclude that after NO adsorption on O-covered unpromoted Ag and Cs-promoted Ag catalysts or Cs-promoted catalysts which were given an LT pretreatment, nitrate species were formed on the surface. As noted previously, exposure of the CsCl (994) catalyst to NO created no nitrate band, which suggests that surface Cl may block adsorption sites.

With the reduced, unpromoted Ag catalysts, gas-phase N_2O formation was an indication of NO adsorption and dissociation. In addition, an 1165 cm^{-1} band occurred after NO adsorption on the UNP-I catalyst reduced at 673 K, and this band can be assigned to the O–O stretching mode of O_2^- because after ^{15}NO adsorption on this catalyst, no red-shift was observed for this band.

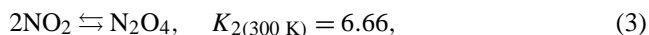
Table 5
Infrared band assignments for NO adsorbed on $\alpha\text{-Al}_2\text{O}_3$ -supported Ag at 300 K

Observed wavenumber (cm^{-1})	Assignment	Based on	Reference
1160–1165	Superoxide (O_2^-)	^{15}NO and O_2 studies	[46–49]
1232–1238	Chelating nitrito	^{15}NO	[49,50]
1396–1420	Surface nitrate	Coadsorption of NO and O_2 and ^{15}NO studies	[45,49]
1317–1474	Bulk Ag nitrate (after coadsorption of NO and O_2)	XRD, IR spectrum of bulk Ag nitrate	[64]

Bands at 2153 and 1117 cm^{-1} were observed after NO adsorption at 300 K on CsN (1175) reduced at 673 K followed by heating to 673 K. The band at 2153 cm^{-1} can be assigned to NO^+ , while the band at 1117 cm^{-1} can be attributed to the O–O stretching mode of O_2^- , shifted presumably due to the Cs on the surface. Because the intensity of these bands increased simultaneously with a decrease of the 1237 cm^{-1} band intensity, it is presumed that these species formed as the chelating nitrito species decomposed on the surface. Infrared band assignments for NO adsorbed on Ag at 300 K are given in Table 5.

4.2. Coadsorption of NO and O_2 at 300 K

Vibrational spectroscopy techniques have been used more extensively for NO_2 adsorption on Ag, and Table 6 summarizes the IR absorption features of NO_x species. These studies have indicated that the formation of NO_3^- species occurred regardless of the temperature range or the form of Ag. NO adsorption on a reduced Ag surface in the presence of oxygen produced gas-phase NO_2 giving an intense peak at 1616 cm^{-1} . A temperature-dependent equilibrium exists between NO_2 and its gas-phase dimer, N_2O_4 [63], i.e.,



with N_2O_4 giving bands at 1750 and 1270 cm^{-1} . Both reactions are reversible and thermodynamic equilibrium shifts to the right at lower temperatures [63]. After flowing this (3% NO + 30% O_2) mixture over the Ag catalysts for 30 min at 300 K, no NO peak was observed because the excess oxygen allowed the conversion of essentially all the NO to NO_2 . Polzonetti et al. investigated the adsorption and reaction of NO_2 on Ag (111) at temperatures of 25, 90, and 300 K and found that adsorption is entirely dissociative at 300 K, giving adsorbed NO and O species which strongly interact, in addition to some NO desorption [28,29]. Outka et al. observed NO_2 and NO_3^- species when NO_2 adsorbed on Ag (110), with part of the chemisorbed NO_2 giving a band at 1165 cm^{-1} and desorbing at 270 K, while NO_3^- was the most stable species [25]. Zemlyanov and co-workers investigated the reaction between Ag foil and a mixture of NO + O_2

Table 6
Reported frequencies of adsorbed NO_x species observed on Ag

Compound	Form of Ag	Form of NO _x	System ^a	Temperature (K)	Vibration	ν (cm ⁻¹)	Reference
NO	Ag powder	NO, NO ₂	SERS		ν_a	1285	[23]
NO ₃ ⁻					γ ONO	815	
					ν NO	1045	
					ν_S	1360	
					ν_a	1605	
NO ₂ ⁻	Ag Powder	NO ₂ /N ₂ O ₄	SERS	293–353	γ ONO	819	[24]
NO ₃ ⁻					ν NO	1040	
NO	Ag (110)	NO ₂	EELS	95–355		1930	[25]
N ₂ O ₄					ν_a	1745	
					γ ONO	795	
NO ₃ ⁻					ν_S	1390	
					ν_S	1555 (weak)	
NO	Ag films	NO, NO ₂	SERS	30–40		1876	[30]
NO ₂ ⁻					ν_a	1263	
					γ ONO	806, 840	
					ν NO	1279	
N ₂ O					ν NN	2222	
					ν NO	1037	
					γ ONO	705	
					ν_a	1341	
NO ₃ ⁻					ν_S , antiphase	1267	
					ν_S , inphase	1382	
					ν_a	1718	
					γ NO	810	
					ν_a	1940	
N ₂ O ₄	Ag (111)	NO ₂	RAIRS	86		1860–1880	[31]
NO						1860–1880, 1590, 1285, 774	
(NO) ₂						1590, 1265, 1045, 761	
N ₂ O ₃						1717–1766, 1305, 774	
NO ₃							
N ₂ O ₄							
NO ⁺	Ag-ZSM-5	NO and O ₂	IR	RT		2140	[19]
N ₂ O ₃						1880, 1590	
N ₂ O ₄						1748	
Chemisorbed NO ₂						1676	
Physisorbed NO ₂						1607	
NO ₃ , bridged						1630	
NO ₃ , bidentate						1576	

^a SERS, surface enhanced Raman spectroscopy; EELS, electron energy loss spectroscopy; IR, infrared spectroscopy.

at 300 K using XPS, ISS, and SEM to identify a complicated sandwich structure consisting of superimposed AgNO₃ and Ag₂O layers at the surface of metallic Ag [35,36,38,39]. In our study, bands due to nitrate were obtained (Fig. 8), and the TPD results were consistent with the DRIFT spectra (Fig. 10a). The nitrate species formed was very stable and decomposed to give NO, O₂, N₂O, and N₂ peaks between 635 and 660 K for all samples. To gain additional information about the form of nitrate, an XRD analysis was conducted with UNP-II, and XRD patterns are shown in Fig. 13 for both fresh UNP-II and UNP-II after exposure to a mixture of NO and O₂ at 300 K. For both samples, the principal peaks for Ag and α -Al₂O₃ were observed; however, for the latter, additional AgNO₃ peaks were also present, which shows that bulk Ag nitrate formation is significant. In fact, the IR bands obtained after coadsorption of NO and O₂ on unpromoted Ag catalysts, shown in Fig. 8, are very similar to an IR spectrum for AgNO₃ [64]. It is difficult to see the

effect of Cs and Cl because prominent IR features due to Ag nitrate dominated for all supported Ag catalysts. The inset in Fig. 8b shows a spectrum of alumina after the introduction of a mixture of NO and O₂, and it reveals bands between 1585 and 1300 cm⁻¹ which may be associated with nitrite species because no TPD for O₂ peak was detected. Recently, Bao et al. studied coadsorption of NO and O₂ on a Ag (110) surface using XPS, UPS, and Raman spectroscopy, and they found that the existence of oxygen enhances the adsorption of NO_x species [37]. When they introduced a 1:10 mixture of NO + O₂ at 375 K, both NO₂ and NO₃⁻ species were formed, and Bao et al. reported that NO acted as a promoter and led to cleavage of oxygen bond and that a surface NO–O₂ complex decomposed at 625 K, a result very similar to ours. In fact, our results show that O₂ desorption peaks were observed around 530–560 K when only O₂ was adsorbed (Fig. 11), whereas the O₂ desorption peak occurred around 630–660 K after coadsorption of NO and O₂ (Fig. 10a),

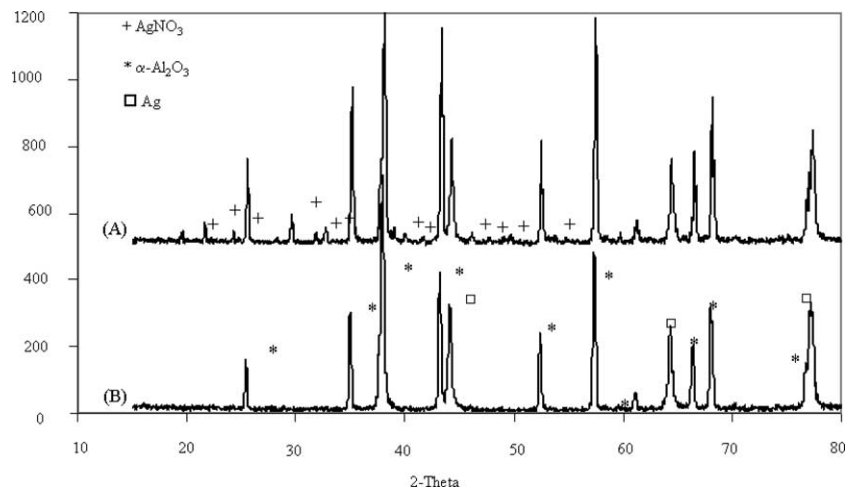


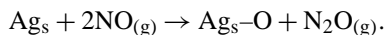
Fig. 13. XRD patterns: (A) UNP-II exposed to a NO/O₂ mixture (22:220 Torr) at 300 K; (B) fresh UNP-II.

which indicates that in the presence of NO, a different form of surface oxygen species exists which has a stronger interaction with the Ag surface.

4.3. NO adsorption at 300 K

Fig. 14 shows DRIFT spectra after NO adsorption on supported Ag catalysts and Cs/alumina at 300 K following a I-LT pretreatment. No significant IR features occurred with the unpromoted catalysts; however, the intensity of the 1232 cm⁻¹ band due to chelating nitrito increases slightly as exposure time increased. Both NO₂⁻ and NO₃⁻ species were observed on the Cs-promoted Ag catalyst, as indicated by the respective band at 1238 and the shoulder at 1345 cm⁻¹, while NO₂⁻ was the only significant N-containing surface species with CsCl (994). It is possible that Cl blocks sites for NO dissociation in the latter catalyst; therefore, surface oxygen required for the formation of NO₃⁻ species was not present.

With samples reduced at 673 K, no nitrate species were observed after a 30-min NO exposure (Fig. 15). For the unpromoted Ag catalysts, only a band near 1165 cm⁻¹ due to the O–O stretching of O₂⁻ was observed, which suggests that NO dissociation occurred on the Ag catalyst; however, no oxidation product was observed and only gas-phase N₂O was detected. NO and O₂ uptake measurements showed that an NO/O_{ad} ratio close to unity was obtained for the unpromoted catalysts; consequently, it is proposed that NO dissociates on the reduced Ag catalysts to form principally Ag–O sites, i.e.,



This reaction could occur either by dissociative NO adsorption followed by N₂O formation or by the initial formation of (NO)₂²⁻ dimers followed by rapid decomposition to give N₂O [6,32]. However, in the current study, there was no spectral evidence for the formation of (NO)₂²⁻ groups following NO adsorption. After N₂O desorption, the remaining

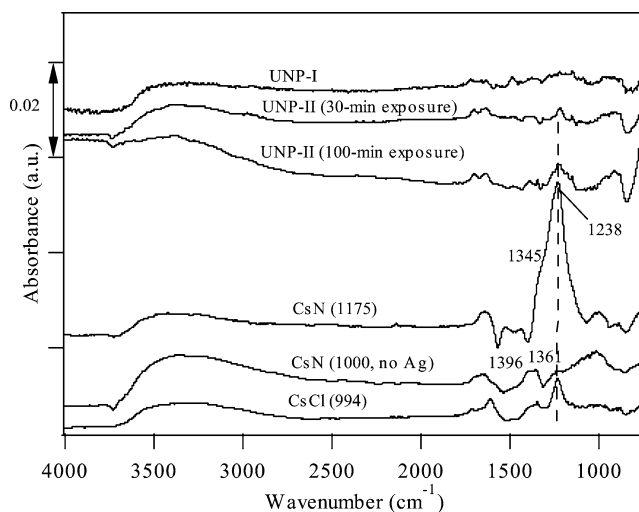


Fig. 14. DRIFT spectra of NO adsorbed at 300 K for a 30-min (unless otherwise stated) at 300 K after a I-LT pretreatment.

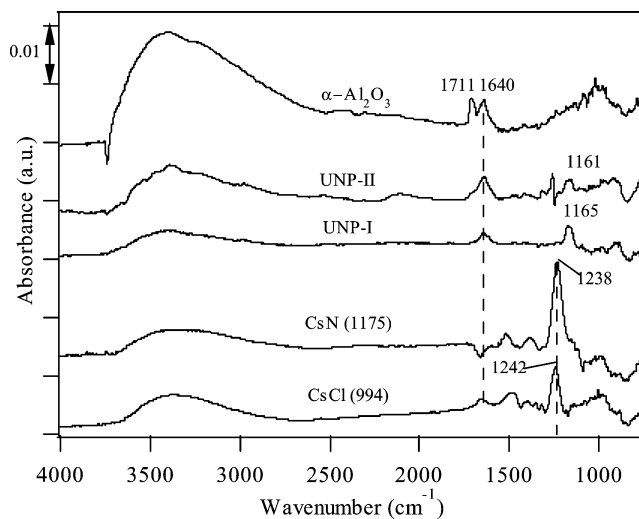


Fig. 15. DRIFT spectra of NO adsorbed at 300 K after a I-HT pretreatment (all spectra were taken after a 30-min purge).

Ag_s–O sites are similar to the sites produced after O₂ adsorption at 443 K.

Bao et al. found that the existence of surface oxygen enhances the adsorption of NO_x [37]; therefore, this could explain the enhanced formation of NO₂[–] on all the Cs-promoted Ag catalysts and the formation of nitrate on the LT- and II-HT-pretreated CsN (1175) samples; i.e., the presence of Cs alters the adsorption behavior of NO and the oxygen chemistry on the surface. These results imply that more surface oxygen should exist on the CsN (1175) catalyst, which is consistent with previous results showing that the reversible O₂ uptake increased by about 30% although the irreversible uptake did decrease [41]. In addition, as shown in Fig. 11, the desorption peak for O₂ was 30 K lower for CsN (1175) than for the unpromoted Ag catalyst, which shows that O₂ is more weakly adsorbed on CsN (1175) than on UNP-II. Consequently, it is hypothesized that Cs facilitates NO dissociation to oxidize metallic Ag sites and form NO₂[–] (1238 cm^{–1}) and NO₃[–] (1345 cm^{–1}) species. Lambert and co-workers have reported that, in the presence of Na, NO was more strongly adsorbed and underwent surface dissociation to yield adsorbed O and N atoms whose subsequent reactions led to the formation of N₂, N₂O, and O₂ as gaseous products, whereas nondissociative NO adsorption occurred on a clean Ag (111) surface [22]. This was attributed to Na being an electron donor, thus increasing the bond strength of adsorbed NO [21,22]. The DRIFTS results here are consistent with the chemisorption studies. With the reduced Cs-promoted Ag catalysts, the NO uptake increased, the CsN (1175) catalyst had a NO_{ad}/O_{ad} ratio of 2.0, and no nitrate species were formed. These results are consistent with the presence of composite AgCs_xO_y sites [1]. It has been discussed previously that after a HT-pretreatment, redistribution of Cs may occur at 673 K to form islands of Ag atoms separated by Cs atoms [1], which might inhibit the formation of nitrate species, and Goncharova et al. have reported that Cs can decrease the concentration of nucleophilic oxygen on a Ag surface [65].

5. Summary

NO adsorption was examined on supported and promoted Ag catalysts to gain insight into the nature of adsorption sites and the effect of Cs and Cl promoters. At 300 K NO dissociates on reduced silver catalysts by oxidizing metallic silver surface atoms and desorbing N₂O. Chemisorption results and DRIFT spectra indicated that Ag–O sites were formed on unpromoted catalysts during NO adsorption after reduction at either 473 or 673 K. The concentration of nitrite species was time dependent and a weak band at 1232 cm^{–1} due to a chelating nitrito species was observed for an unpromoted Ag catalyst following reduction at 473 K and longer exposures times. After reduction at 673 K, chemisorption of O₂ to give a monolayer coverage, and exposure to NO, nitrate species were formed on the unpromoted catalysts,

as indicated by a band at 1396 cm^{–1}. The intensity of the band due to chelating nitrito increased considerably for the Cs-promoted Ag catalysts. This was not due to NO adsorption on Cs sites, which was demonstrated by experiments with a Cs/Al₂O₃ sample, but rather was related to a change in chemical behavior of the surface oxygen associated with Cs. After reduction at 473 K of CsN (1175), which contained no Cl, and the formation of an oxygen monolayer, nitrate species were formed during NO adsorption. In contrast, exposure of this catalyst to NO after reduction at 473 K produced both nitrate and nitrite species, but only the latter species were observed after NO exposure following reduction at 673 K. This was attributed to redistribution of Cs, due to the higher temperature in the latter case, which decreased the nucleophilic oxygen on the surface associated with the formation of nitrate species. Surface Cl blocked Ag sites and prevented nitrate formation on CsCl (994); however, similar to CsN (1175), a chelating nitrito species was formed on this catalyst regardless of the pretreatment. The presence of adsorbed oxygen enhanced NO_x interaction with the Ag surface and, after O₂ and NO coadsorption, this adsorbed oxygen was more strongly bound on the Ag surface.

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