Available online at www.sciencedirect.com

SCIENCE @ DIRECT®

Journal of Catalysis 222 (2004) 214–226

JOURNAL OF CATALYSIS

www.elsevier.com/locate/jcat

Adsorption of 1,3-butadiene on supported and promoted silver catalysts

Jale Müslehiddinoğlu and M. Albert Vannice *

Department of Chemical Engineering, 107 Fenske Laboratory, The Pennsylvania State University, University Park, PA 16802-4400, USA

Received 28 July 2003; revised 31 October 2003; accepted 31 October 2003

Abstract

After exposure to 1,3-butadiene, unpromoted Ag/α-Al_2O_3 and Ag/α-Al_2O_3 promoted with Cs and Cl were characterized using DRIFTS. Weakly adsorbed molecular butadiene was the dominant species for all samples regardless of the adsorption temperature. After purging alumina with He, no IR absorption features remained with alumina, whereas spectra showed that butadiene adsorbed irreversibly at 300 K via one of its C=C bonds on either the reduced or O-covered unpromoted Ag surface which led to a surface species resembling 1,2-butadiene, and on the O-covered Ag surface, crotonaldehyde and carbonaceous species were also present. The formation of these carbonaceous species on an O-covered Ag catalyst implied that chemisorbed oxygen facilitates additional C–H bond breaking. On Cs-promoted Ag/α-Al_2O_3 covered with a monolayer of oxygen following reduction at 673 K, a dehydrogenated 1,2-butadiene-type surface species appeared to exist at 300 K in addition to other carbonaceous species. Isotope studies revealed that 1,3-butadiene adsorbs through both C=C bonds on a Cs-promoted Ag catalyst and may exist as an oxametallacycle intermediate requiring two types of sites, i.e., an unpromoted Ag site and a Cs-promoted Ag site containing surface oxygen. In the presence of Cl, 1,3-butadiene was weakly adsorbed on the Ag surface at 300 K through a single C=C bond regardless of the presence or absence of chemisorbed oxygen. DRIFT spectra obtained under epoxidation reaction conditions at 473 K and 1 atm indicated that 1,3-butadiene dehydrogenated on alumina alone to give carbonaceous species, whereas carboxylate compounds were the principal species on both unpromoted and promoted Ag catalysts, although crotonaldehyde was also observed. No epoxybutene was detected.

Keywords: 1,3-Butadiene; Silver; Ag/α-Al_2O_3 DRIFTS; Cs; Cl; Epoxybutene; Epoxidation

1. Introduction

Silver is a uniquely effective catalyst for direct olefin epoxidation reactions involving unsaturated hydrocarbons with no allylic hydrogen atoms [1–5]. In ethylene, the vinylic C–H bond strength is extremely strong ($D = 102$ kcal/mol), whereas the allylic C–H bond in propylene, for example, is much weaker ($D = 85$ kcal/mol) [6]; hence, abstraction of an allylic H atom from propylene by oxygen is more favorable than an electrophilic attack on the olefin double bond to give propylene oxide. Once hydrogen abstraction begins, the thermodynamically favorable route of combustion is preferred and epoxide formation is precluded. This explanation accounts for the extremely low epoxidation selectivities of propylene, 1-butene, and 2-butene [5,7] and the highly selective epoxidation of styrene [5,8–10], 3,3-dimethylbutene [7,11], norbornene [5,9,12], and 1,3-butadiene (BD). The last reaction is the second example of a commercial epoxidation process using hydrocarbon and dioxygen [5,7,9,13–16].

As with ethylene epoxidation to ethylene oxide, the epoxidation of BD to epoxybutene (EpB) utilizes a silver-based catalyst; however, the composition of the catalyst in terms of the loading of promoters is different from that typically used for ethylene oxide. For example, catalysts optimized for EpB production incorporate a much higher loading of Cs than those optimized for ethylene oxide production, i.e., 900–1000 ppm versus 200–300 ppm [9]. To better understand the compositional features of the BD epoxidation catalysts and to elucidate the interactions between BD and these promoted Ag catalysts, diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was used to examine the adsorption and reaction of BD at 300 and 473 K on unpromoted α-Al_2O_3-supported Ag as well as this catalyst promoted with Cs and Cl.

Vibrational spectroscopic methods frequently have been applied to identify adsorbed species on metal surfaces and to probe the nature of adsorption sites; however, there have been only limited studies of BD adsorption on Ag surfaces

---

* Corresponding author.
E-mail address: mavche@engr.psu.edu (M.A. Vannice).

0021-9517/$ – see front matter © 2003 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcat.2003.10.023

and no reports pertaining to BD on supported Ag catalysts. Previous work with Ag (111) at 25–30 K using infrared reflection–absorption spectroscopy (IRAS) determined that BD lies parallel to the surface, and increasing the temperature to 90 K resulted in tilting of the molecular plane with C=C bonds remaining parallel to the surface [17]. Itoh and co-workers showed with both surface-enhanced Raman scattering spectroscopy (SERS) and ab initio molecular orbital calculations that, depending on the temperature, BD may adsorb on positively charged Ag atoms via either a single C=C bond (at 120 K) or both C=C bonds (at 180 K) [18–20]. Madix and co-workers [21] and Schiøtt and Jørgensen [22] studied the reaction of BD with oxygen atoms on Ag (110) using TPD and extended Hückel tight-binding calculations, and they showed that 1,4 addition to give 2,5-dihydrofuran was favored. On the other hand, Monnier and co-workers showed that when BD is adsorbed on dispersed, oxygen-covered Ag crystallites, EpB is formed with high selectivity due to 1,2 addition [5,9,23–25].

Badani et al. measured integral heats of adsorption, Q_{ad}, at 300 K for BD on unpromoted and promoted Ag/α-Al_2O_3 catalysts [26]. Irreversibly adsorbed butadiene was more weakly bound on O-covered surfaces than on reduced Ag surfaces, but the amount of irreversibly adsorbed BD was higher on O-covered catalysts than on reduced catalysts. Addition of a Cs promoter (1175 ppm) lowered both the amount and the Q_{ad} value of irreversibly adsorbed BD, and essentially all the butadiene was reversibly adsorbed in the presence of both Cs and Cl.

In the present study, the adsorption behavior of BD on both unpromoted and promoted Ag/α-Al_2O_3, as well as the alumina support, was investigated. To help identify adsorbed species, isotope experiments were conducted with deuterium-labeled BD (C_4D_6) and $^{18}O_2$.

2. Experimental

Details regarding the preparation and surface characterization of these supported silver catalysts have been given elsewhere [27]. The unpromoted catalyst used in this study is designated as UNP-II. Two nominal 1000-ppm Cs-promoted Ag catalysts, and one Cs/α-Al_2O_3 sample, respectively designated as CsN (1174), CsCl (994), and CsN (1000, no Ag), were used. The prefixes CsN and CsCl indicate whether $CsNO_3$ or CsCl was the precursor Cs compound, and the number in parentheses indicates the analyzed Cs content in ppm as shown in Table 1. The properties of the catalysts are also given elsewhere [27]. In addition to these catalysts, experiments were performed with the pure α-Al_2O_3 support (Norton Corp., SA 5562, 0.78 m^2/g). The samples were subjected to either a low temperature (LT) reduction at 473 K or a high temperature (HT) reduction of 673 K, and the surface was left in either a reduced or an O-covered state, as described in Table 2.

Table 1
Composition of Ag catalysts

Catalyst	Silver (%)	Cesium (ppm)	Chlorine (ppm)	D^a (nm)
UNP-II	14.9	0	0	275
CsN (1175)	10.8	1174	0	354
CsN (1000, no Ag)	0	1000	0	–
CsCl (994)	13.1	994	310^b	–

[a] Based on SEM analysis.
[b] Nominal amount based on Cs content.

Table 2
Catalyst pretreatment procedures

I-LT (HT)-reduced:
(1) Heat from 300 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) Bring sample to either 300 or 473 K
(5) Introduce BD at a total flow of 20 sccm (9% BD and 18% O_2, for isotopes: 68 Torr 1,3-butadiene-D6 (BDD6) and 136 Torr $^{18}O_2$, unless otherwise specified

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 for 30 min
(3) Bring sample to adsorption temperature and introduce BD

Details of the diffuse reflectance FTIR system and the standard procedures employed to record spectra have been described in detail elsewhere [27]. Briefly, after loading the catalyst sample into the DRIFTS cell, the cell was purged overnight with He. The sample was then subjected to one of the in situ pretreatments and cooled to either 300 or 473 K, at which point the first interferogram was taken. This was used as the background reference in the fast Fourier transform analysis of all the subsequent interferograms recorded for that particular catalyst. As before, the spectra in absorbance units or K–M units were very similar, but we prefer to show the former because negative changes in the spectrum are also observable [27]. Afterward, the adsorbate was flowed through the catalyst bed in a He carrier gas (or isotopes were introduced to the evacuated cell) for 30 min and IR scans were taken after 30 min. The catalyst was then purged with 20 sccm He for 30 min after which time another scan was taken.

The nonhydrocarbon gases used were He (99.999%, MG Ind.), O_2 (99.999%, MG Ind.), H_2 (99.999%, MG Ind.), and $^{18}O_2$ (99.2%, Matheson). Except for $^{18}O_2$, all these gases were passed through drying tubes, and He and H_2 were also passed through Oxytraps (Alltech Assoc.). The hydrocarbon gases, i.e., 1,3-butadiene (99.0%, MG Ind.) and 1,3-butadiene-D6 (BDD6) (98%, Cambridge Isotope Lab.) were used without further purification.

3. Results

3.1. 1,3-Butadiene adsorption at 300 K

Fig. 1 displays spectra obtained for BD after adsorption on alumina and supported Ag samples following a I-LT pretreatment and exposure to 68 Torr BD at 300 K. After subtraction of the gas-phase BD spectrum from each spectrum, the bands observed were similar to those obtained for gas-phase BD, thus implying that weakly adsorbed BD is the principal species on both alumina and Ag during BD exposure. The 1011 cm^{-1} band, which is due to $\rho(CH_2)$, was not observed with alumina, as shown in the first spectrum in Fig. 1; however, the surface Al–O–Al bridges which give bands in the 1020 to 1060 cm^{-1} spectral region might be perturbed due to the interaction between alumina and BD and interface with the detection of the 1011-cm^{-1} band [28,29, and references therein].

The first IR spectrum in Fig. 2 was taken after exposure of alumina to 68 Torr BD at 300 K following a I-LT pretreatment and a 30-min purge. A 1641-cm^{-1} band is attributed to chemisorption of trace amounts of water [30,31]. This band was also observed for all of the supported Ag catalysts so to remove it, the spectrum obtained with alumina after each pretreatment was subtracted from those obtained with the supported Ag catalysts. The negative band at 3740 cm^{-1} is assigned to a terminal (isolated) OH group over an octahedrally coordinated Al ion, while the broad band between 3470 and 3370 cm^{-1} is assigned to bridging OH-stretching modes [32]. The negative band appearing at 3740 cm^{-1} indicates a loss of isolated OH groups due to the adsorbate. The intensity increase for the bridging hydroxy groups may be a result of either an interaction between the adsorbate and the alumina surface or the formation of additional hydroxy groups. It is difficult to determine whether additional hydroxy groups were formed during adsorption because the extinction coefficient of the hydroxy groups increases with their concentration [33]. Although volumetric studies indicated no significant irreversible adsorption on the α-Al_2O_3 support [26], to clarify whether C–H cleavage occurs on the alumina surface to form additional bridging hydroxy groups, BDD6 was adsorbed on alumina at 300 K after a I-LT pretreatment, as shown in Fig. 2. No OD-stretching bands were detected in the 2600 to 2750 cm^{-1} spectral region, indicating that no C–H (D) cleavage occurred on the alumina.

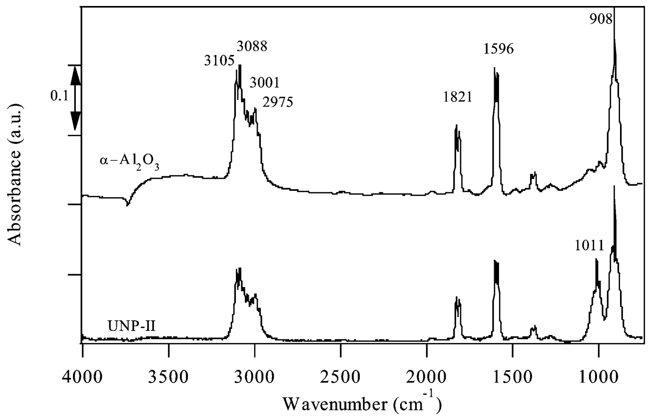


Fig. 1. DRIFT spectra of 1,3-butadiene (BD) adsorbed at 300 K after reduction at 473 K; gas-phase BD spectrum was removed.

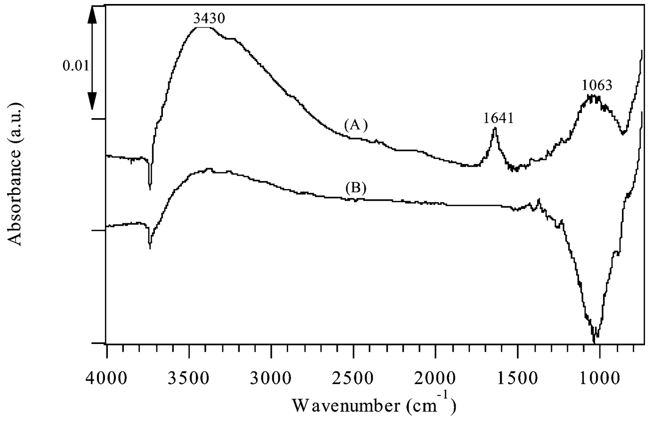


Fig. 2. DRIFT spectra of: (A) C_4H_6 or (B) C_4D_6 adsorbed on α-Al_2O_3 at 300 K after a reduction at 473 K following a 30-min purge.

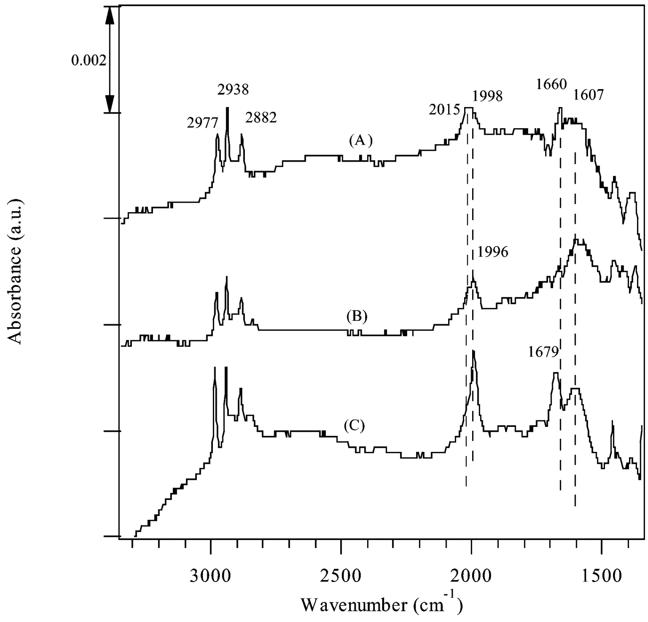


Fig. 3. DRIFT spectra of BD adsorbed on UNP-II at 300 K (A) after a I-LT pretreatment; (B) after a II-LT pretreatment; (C) in the presence of 136 Torr O_2 after a I-LT pretreatment; all spectra taken after purging for 30 min.

Fig. 3 provides DRIFT spectra for BD adsorption on the UNP-II catalyst at 300 K after either a I-LT or a II-LT pretreatment. IR bands occurred at 2977, 2938, 2882, and around 2000 cm^{-1} on both the reduced and the O-covered Ag surfaces that resembled those of gas-phase 1,2-butadiene; therefore, primarily because of the last band, the surface structure of this species was assumed to have 1,2-BD-type characteristics and is called “1,2-BD-type.” The assignment of vibration modes is given in Table 3 [34–45]. It is stressed that this adsorbed species is not molecular 1,2-butadiene because the isomerization of 1,3-butadiene to 1,2-butadiene is

Table 3
Vibrational mode assignments for 1,2-butadiene, carboxylate, and carbonaceous compounds

Mode	Gas-phase 1,2-butadiene[a]	COO^{-} [b]	Carbonaceous[c] compounds
$\nu_a(=CH_2)$	3012		
$\nu_a(CH_3)$	2977–2990		
$\nu_s(CH_2)$	2930–2950		
$\nu_s(CH_3)$	2874–2880		
$\nu(C=C=C)$	1957		
$\nu(C=C)$			1575–1600
$\nu_a(COO)$		1560–1630	
$\nu_s(COO)$		1350–1420	
$\delta(CH_2/CH_3)$	1453, 1430	1042	
$\nu(C–C)$			1400–1420
$w(CH_2)$	908		

ν, stretch; w, wagging; δ, deformation; a, asymmetric; s, symmetric.
[a] Refs. [34,35].
[b] Refs. [36–38].
[c] Refs. [39–45].

thermodynamically unfavorable, with an equilibrium conversion of 4×10^{-9} [46,47]. The broad band between 1990 and 2020 cm^{-1} is attributed to cumulative C=C-stretching vibrations in the surface species formed on reduced and O-covered UNP-II. After exposure of UNP-II to BD in the presence of O_2 ($BD:O_2$, 1:2) the intensity of bands at 2977, 2938, 2882, and 1996 cm^{-1} increased, as shown in the third spectrum in Fig. 3 and bands at 1679 and 1607 cm^{-1} were also observed. The former band can be assigned to the C=O-stretching mode of crotonaldehyde, as discussed later in this section, while the latter may be ascribed to C=C-stretching modes in a carbonaceous species, as explained later.

On the unpromoted catalyst reduced at 673 K, BD adsorption appeared to form the same adsorbed species as that on the sample reduced at 473 K (Fig. 4). Spectrum A in Fig. 4 was taken after a 30-min purge following BD adsorption at 68 Torr on I-HT-pretreated UNP-II, and it indicated a 1,2-BD-type surface species. After a II-HT pretreatment, the intensity of these bands increased, as shown in spectrum B in Fig. 4, and bands at 1658 and 1598 cm^{-1} appeared due to crotonaldehyde and the C=C modes in a carbonaceous species, respectively. Spectrum C in Fig. 4 shows BD adsorption on ^{18}O-covered UNP-II at 300 K. If the band at 1993 cm^{-1} were due to CO or butadiene interacting with surface oxygen, a red shift would be expected; however, none occurred, thus supporting the proposal that the 1993-cm^{-1} band is due to C=C=C-stretching modes of an adsorbed species interacting with Ag sites. To gain insight into the effect of Cs, experiments were conducted not only with CsN (1175) but also with $Cs/\alpha\text{-}Al_2O_3$, which gave no IR features due to BD adsorption [47]. The DRIFT spectra of promoted $Ag/\alpha\text{-}Al_2O_3$ catalysts taken after a 68-Torr BD exposure were similar to those observed for UNP-II, i.e., the principal species was reversibly adsorbed BD [47].

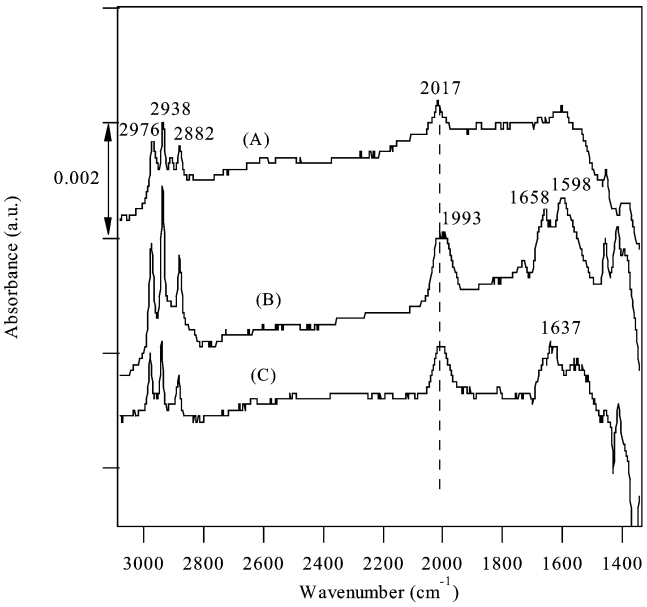


Fig. 4. DRIFT spectra of BD adsorbed on UNP-II at 300 K (A) after a I-HT pretreatment; (B) after a II ($^{16}O_2$)-HT pretreatment; (C) after a II ($^{18}O_2$)-HT pretreatment. Spectra taken after a 30-min purge.

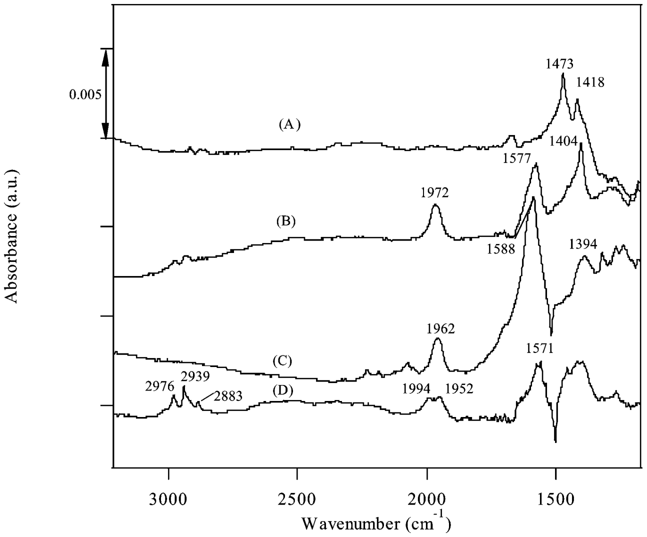


Fig. 5. DRIFT spectra taken at 300 K for CsN (1175): (A) BD adsorbed after a I-HT pretreatment; (B) BD adsorbed after a II ($^{16}O_2$)-HT pretreatment; (C) BDD6 adsorbed after a II ($^{16}O_2$)-HT pretreatment; (D) BD adsorbed after a II ($^{18}O_2$)-HT pretreatment. Spectra taken after a 30-min purge.

Fig. 5 shows spectra taken at 300 K with CsN (1175) after reduction at 673 K, and a dominant band appeared at 1473 cm^{-1} along with another band at 1418 cm^{-1}, as shown in spectrum A. The band at 1473 cm^{-1} red-shifted to 1404 cm^{-1} after BD adsorption on the O-covered surface as shown in spectrum B and, in addition, a band was created at 1577 cm^{-1} along with another at 1972 cm^{-1}, and very weak bands were observed in the CH_x-stretching region. To clarify the assignment of these bands, isotopically labeled BD and $^{18}O_2$ were used. BDD6 was adsorbed on ^{16}O-covered CsN (1175) (spectrum C), and then BD was adsorbed on ^{18}O-covered CsN (1175) (spectrum D). These spectra in Fig. 5 were taken following a 30-min purge. After BDD6 adsorption, weak bands were observed at 2230, 2186, and 2076 cm^{-1} due to C–D-stretching bands, which are the counterparts of the CH_2/CH_3-stretching modes at 2979, 2938, and 2883 cm^{-1}, as shown in the third spectrum C. The band at 1972 cm^{-1} was red-shifted slightly to 1962 cm^{-1} after BDD6 adsorption, which indicates that this band could be due to C=C-stretching modes of a 1,2-BD-type species because it has been reported that the C=C-stretching band in deuterated allene ($CD_2{=}C{=}CD_2$) is red-shifted about 36 cm^{-1} [48]. The 1577-cm^{-1} band was not red-shifted after BDD6 adsorption which implies that this band was due to dehydrogenated adsorbed species. To clarify this band, BD was adsorbed on ^{18}O-covered CsN (1175), as shown in spectrum D in Fig. 5, and a slight red shift was observed to 1571 cm^{-1}. If this band were due to a COO^--stretching mode, it would have shifted more, i.e., about 20–30 cm^{-1} [49]. This suggests that the band at 1577 cm^{-1} was due to a C=C-stretching mode of dehydrogenated carbonaceous species, similar to that observed on UNP-II. In contrast to BD adsorption on ^{16}O-covered CsN (1175), BD adsorption on the ^{18}O-covered sample provided CH_x-stretching bands with significant intensity, the 1972 cm^{-1} band shifted to 1952 cm^{-1} implying that the 1,2-BD-type species binds to surface oxygen, and another band was detected at 1994 cm^{-1} that was also assigned to a C=C-stretching mode in this species. Finally, the band at 1404 cm^{-1} red-shifted to 1394 cm^{-1} after BDD6 adsorption on the ^{16}O-covered sample; however, it did not shift after BD adsorption on the ^{18}O-covered sample. This band is assigned to weakened C=C-stretching modes in a dehydrogenated olefinic species because the band would be red-shifted at least 100 cm^{-1}, if it were not dehydrogenated [34]. As noted earlier, on the reduced sample this band appeared at 1473 cm^{-1}, implying that the presence of oxygen on the Cs-promoted surface may weaken the C=C bond; thus, the band red-shifted as the oxygen coverage increased.

To examine the effect of Cl, BD was adsorbed on CsCl (994) at 300 K after either a I-LT or a II-LT pretreatment and spectra were taken after a 30-min purge, as shown in Fig. 6. The reduced sample gave only one band at 1629 cm^{-1}, which was due to the ν(C=C) mode of adsorbed BD. With the O-covered sample, weak bands were observed in the $\nu(CH_x)$ region, along with a broad band near 1606 cm^{-1}, assigned to either the C=C-stretching mode of BD or a $\nu_a(COO^-)$ mode in a carboxylate group, and a band at 1390 cm^{-1}, assigned to the $\nu_s(COO^-)$ mode in a carboxylate group.

3.2. 1,3-Butadiene adsorption at 473 K

Fig. 7 displays IR spectra for BD adsorption at 473 K on alumina and unpromoted Ag/α-Al_2O_3 in the presence of O_2 after reduction at 473 K and a 30-min purge. Adsorbed crotonaldehyde with a ν(C=O) band at 1659–1668 cm^{-1} and dehydrogenated carbonaceous species with a ν(C=C) band at 1592 cm^{-1} were observed on both samples, while the 1397-cm^{-1} band was due to the $\nu_s(COO^-)$ mode of carboxylate species formed on the Ag surface; therefore, the 1592-cm^{-1} band may also have a contribution from the COO^- asymmetric stretching mode in carboxylate groups, as discussed later for samples reduced at 673 K.

Figs. 8a and 8b show spectra taken for BD and BDD6 adsorption at 473 K in the presence of $^{16}O_2$ or $^{18}O_2$ on either α-Al_2O_3 or unpromoted Ag/α-Al_2O_3 after a I-HT pretreatment. The top spectrum in Fig. 8a is similar to that obtained with LT-pretreated alumina. The spectrum taken after BDD6 adsorption in the presence of $^{16}O_2$ displays bands at 2752 and 2601 cm^{-1} attributed to free and bridged O–D-stretching vibration modes, showing that C–D cleavage occurred on the alumina surface (Fig. 8a). This is consistent with the formation of dehydrogenated carbonaceous species indicated by the absence of a red-shift in the band position at 1599 cm^{-1} after adsorption of BDD6 or BD adsorption in the presence of $^{18}O_2$. If the band at 1599 cm^{-1} were not due to dehydrogenated species, a 80- to 100-cm^{-1} shift would have been expected [34]. Similarly, the band at 1398 cm^{-1} did not red-shift after isotope experiments.

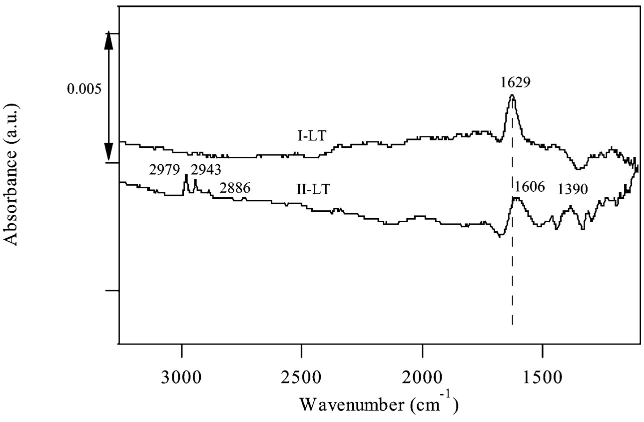


Fig. 6. DRIFT spectra of BD adsorbed at 300 K on CsCl (994) after a 30-min purge following 68 Torr BD exposure: (A) after I-LT pretreatment; (B) after a II-LT pretreatment.

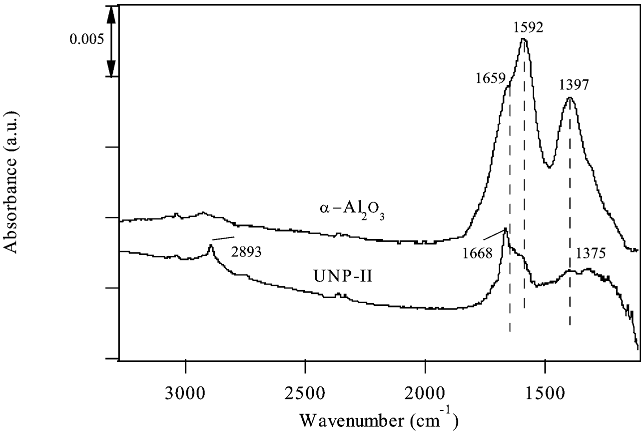


Fig. 7. DRIFT spectra after BD adsorption on Al_2O_3 and unpromoted Ag/α-Al_2O_3 at 473 K in the presence of oxygen (BD:O_2 = 68:136 Torr) following a I-LT pretreatment and a 30-min purge.

One of the most prominent features in the infrared spectra of coal, chars, and other carbon materials is a relatively intense band around 1600–1585 cm^{-1} [39–45], and Blanco and Ferraras have assigned a band around 1405–1420 cm^{-1} to the C–C-stretching modes of aromatics [43]. Moreover, BD and 1-butene adsorption on different catalysts, such as Cu-exchanged zeolites and Cr_2O_3/Al_2O_3, and coke deposits produced a band between 1600 and 1585 cm^{-1} (polyolefinic, aromatics) [44,45]. Consequently, the bands at 1599 and 1398 cm^{-1} are attributed to the respective C=C- and C–C-stretching modes in dehydrogenated carbonaceous species with an aromatic nature. The band at 1667 cm^{-1} shifted to 1657 or 1639 cm^{-1} after coadsorption of BDD6 and $^{16}O_2$ or BD and $^{18}O_2$, respectively, as shown in the middle and lower spectra in Fig. 8a. The C=O-stretching vibration shifts around 10 cm^{-1} in deuterium-labeled aldehyde and 20–30 cm^{-1} for ^{18}O-labeled aldehydes, respectively, [49]; hence, the band at 1667 cm^{-1} is assigned to the C=O group in crotonaldehyde. The band at 2171 cm^{-1} is assigned to a CD_3-stretching mode of crotonaldehyde which is the counterpart of the 2894-cm^{-1} band for this CH_3-stretching mode.

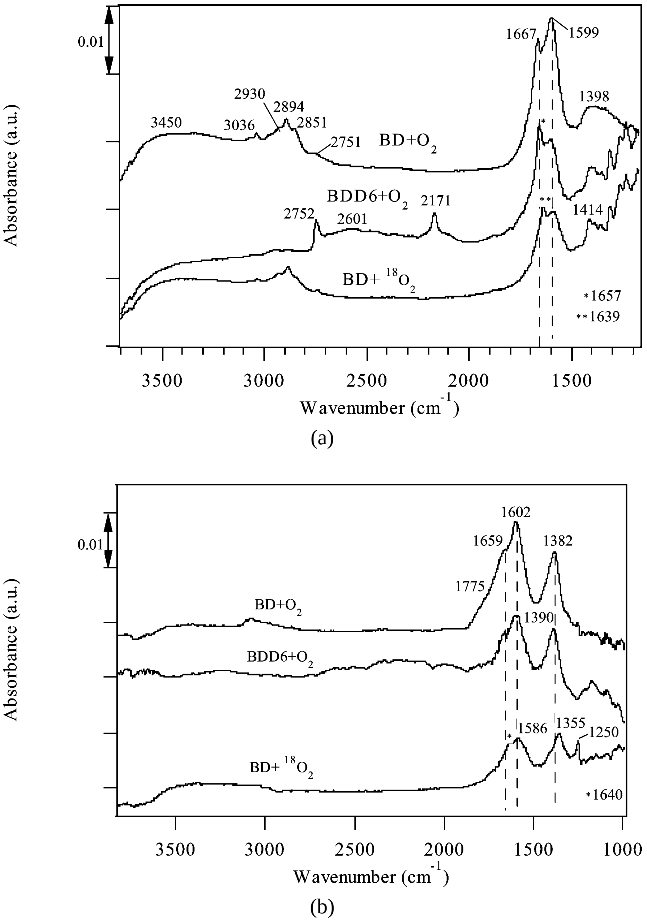


Fig. 8. DRIFT spectra taken at 473 K for (a) α-Al_2O_3; (b) UNP-II after reduction at 673 K (68 Torr BD (or BDD6) and 136 Torr $^{16}O_2$ (or $^{18}O_2$)). Spectra taken after a 30-min purge.

Coadsorption of isotopically labeled BD and O_2 on Ag/α-Al_2O_3 at 473 K showed IR absorption features similar to the spectra obtained for alumina, as shown in Fig. 8b; however, the 1382-cm^{-1} band was not observed with alumina and, although it did not red-shift when BDD6 was adsorbed in the presence of $^{16}O_2$, it did red-shift to 1355 cm^{-1} when BD was adsorbed in the presence of $^{18}O_2$. This is consistent with the assignment to a COO^--stretching mode in a carboxylate species formed on Ag. The band at 1602 cm^{-1} showed only a slight red-shift when BD was adsorbed in the presence of $^{18}O_2$, which may imply that the dehydrogenated carbonaceous species formed on the alumina were mobile and interacted with the O-covered Ag sites to form carboxylate species.

Fig. 9 displays DRIFT spectra of BD adsorbed on Cs/α-Al_2O_3 at 473 K in the presence of O_2 after applying a I-HT pretreatment. In comparison to alumina (Fig. 8a), the relative intensity of the 1640 cm^{-1} band attributed to the

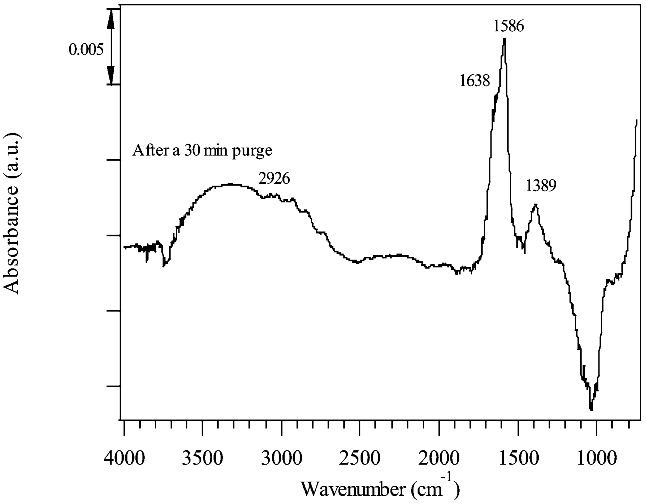


Fig. 9. DRIFT spectra of BD adsorbed in the presence of O_2 on CsN (1000, no Ag) at 473 K after reduction at 673 K.

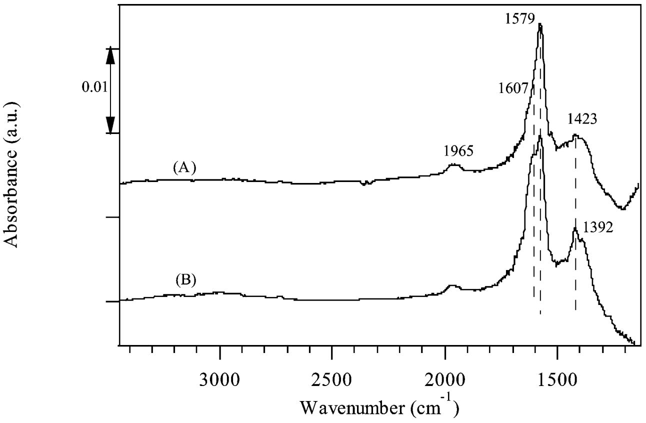
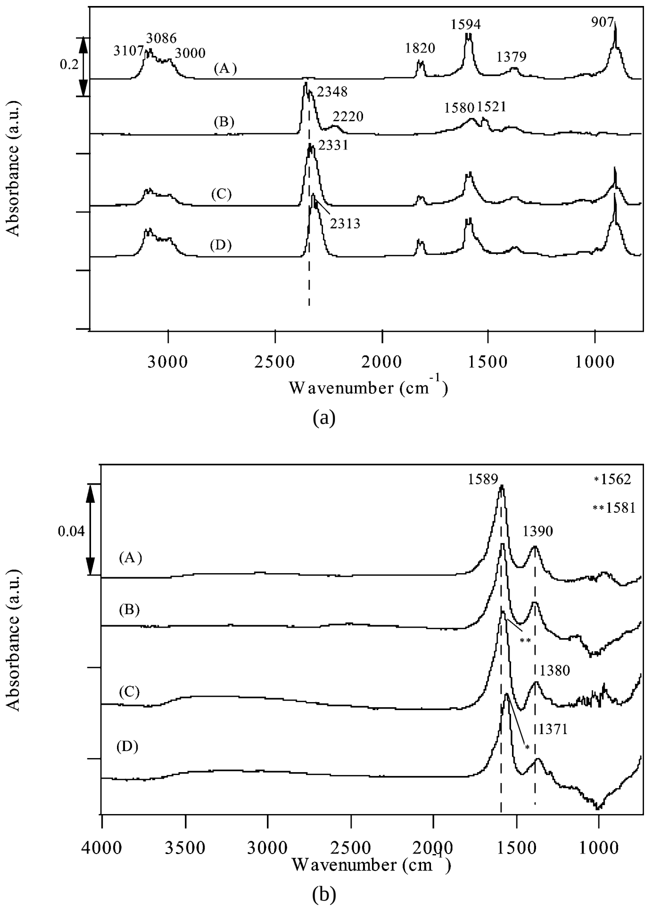


Fig. 10. DRIFT spectra of BD adsorbed in the presence of O_2 on CsN (1175) at 373 K after a I-HT pretreatment; (A) after a 30-min purge following exposure to a 16% BD, 2% O_2 mixture; (B) after a 30-min purge following exposure to a 9% BD, 18% O_2 mixture.

C=O-stretching mode in crotonaldehyde decreased, and, in addition, bands were observed at 1586 and 1389 cm^{-1} that can be assigned to the respective $\nu_a(COO^-)$ and $\nu_s(COO^-)$ modes of a carboxylate group [36–38].

Fig. 10 gives DRIFT spectra after BD adsorption on CsN (1175) at 373 K in the presence of oxygen after reduction at 673 K. Spectrum A was taken after a 30-min purge following a 30-min exposure to 16% BD and 2% O_2 (oxygen lean), while spectrum B was taken after a 30-min exposure to 9% BD and 18% O_2 (oxygen rich) followed by a 30-min purge. In either case, the bands observed were similar. The weak 1965-cm^{-1} band is attributed to a C=C-stretching mode in the dehydrogenated 1,2-BD-type species on CsN (1175). The band at 1579 cm^{-1}, attributed to C=C bonds in carbonaceous species, was observed in either the oxygen-lean or the oxygen-rich environment; however, weak bands at 1607 and 1392 cm^{-1}, assigned to $\nu_a(COO^-)$ and $\nu_s(COO^-)$ modes of carboxylate species, were detected only in the latter.

Figs. 11a and 11b illustrate BD and BDD6 adsorption at 473 K on CsN (1175) in the presence of $^{16}O_2$ and/or $^{18}O_2$ after reduction at 673 K after either a 30-min exposure or a 30-min purge. These mixtures of BD and O_2 were not introduced continuously, yet the limited amount of gas-phase BD (or BDD6) did not completely disappear after a 30-min exposure and reversibly adsorbed BD (or BDD6) was observed after subtracting the gas-phase BD (or BDD6) spectrum (Fig. 11a). Spectrum A in Fig. 11a was taken after a 30-min exposure of CsN (1175) to a mixture of BD and $^{16}O_2$ and, because the mixture was introduced continuously and purged with He, only a small absorption feature due to $C^{16}O_2$ was detected at 2348 cm^{-1} after subtracting the gas-phase BD spectrum, as was reversibly adsorbed BD. Spectrum B in Fig. 1a shows a 2348-cm^{-1} band due to gas-phase CO_2, and this band is in the same spectral region as some C–D-stretching bands. The bands at 2220 and 1521 cm^{-1} are attributed to C–D-stretching and ν(C=C) modes of BDD6, respectively. After introduction of the mixture of BD, $^{16}O_2$, and $^{18}O_2$ (68:68:68 Torr), gas-phase $C^{16}O^{18}O$ was detected at 2331 cm^{-1}, while after introduction of the BD and $^{18}O_2$ mixture, gas-phase $C^{18}O_2$ was observed at 2313 cm^{-1}. All the gas-phase CO_2 disappeared after a 30-min purge, as shown in Fig. 11b, and only bands between 1300 and 1600 cm^{-1} remained. After BD adsorption in the presence of $^{16}O_2$, bands were observed at 1589 and 1390 cm^{-1} and no red-shift was observed for those bands after BDD6 adsorption in the presence of $^{16}O_2$, implying that this adsorbed species did not incorporate any hydrogen. The bands at 1589 and 1390 cm^{-1} red-shifted slightly for the sample exposed to the mixture of BD, $^{16}O_2$, and $^{18}O_2$, while those same bands shifted to 1562 and 1371 cm^{-1}, respectively, for the sample exposed to a mixture of BD and $^{18}O_2$. Thus, the 1589- and 1390-cm^{-1} bands are assigned to $\nu_a(COO^-)$ and $\nu_s(COO^-)$ modes of carboxylate, respectively. BD was also adsorbed on Cs/α-Al_2O_3 and CsN (1175) in the presence of oxygen at 473 K after a I-LT pretreatment and the spectra obtained were similar to those for samples after reduction at 673 K [47], so they are not shown here.



(a)

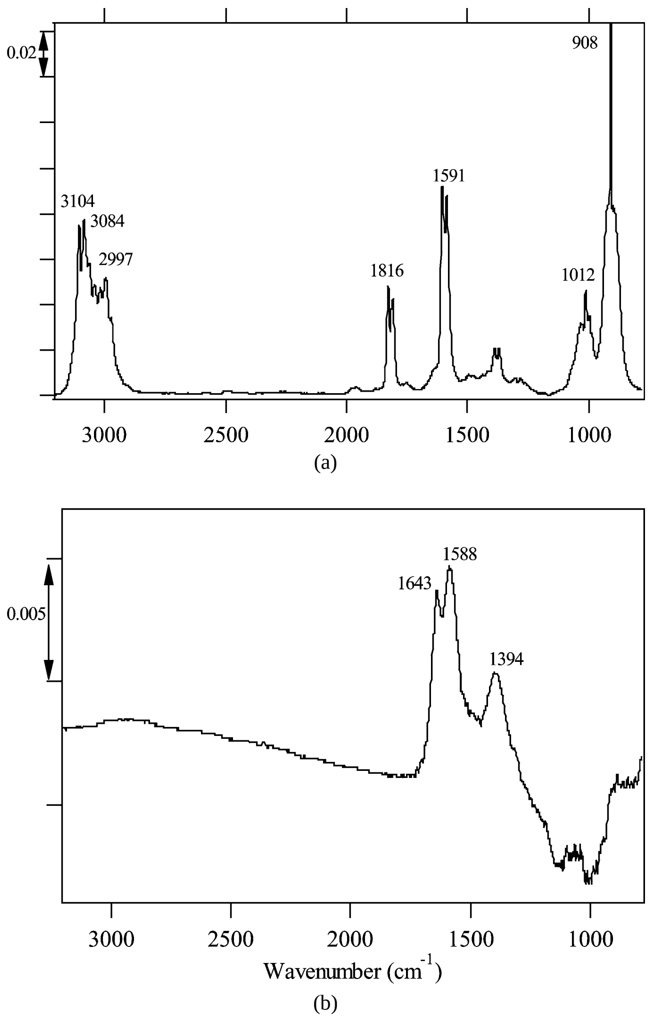
(b)

Fig. 11. DRIFT spectra of BD (or BDD6) adsorbed in the presence of O_2 at 473 K on CsN (1175) after a I-HT pretreatment; (a) during exposure (vapor-phase spectrum subtracted); (b) after a 30-min purge; (A) 30-min exposure to 9% BD and 18% O_2; continuous flow; (B) 30-min exposure to 9% BDD6 and 18% O_2; batch; (C) 30-min exposure to 9% BD, 9% $^{16}O_2$, and 9% $^{18}O_2$; batch; (D) 30-min exposure to 9% BD and 18% $^{18}O_2$; batch.

Fig. 12 shows DRIFT spectra after BD adsorption on CsCl (994) at 473 K in the presence of O_2 after reduction at 473 K. CsCl-promoted Ag/α-Al_2O_3 is a catalyst for which high activity and maximum selectivity to EpB have been achieved [7–9]. As seen in Fig. 12, reversibly adsorbed BD was the dominant species during exposure to BD, and no EpB was detected. Similar to the Cs-promoted catalyst, after a 30-min purge a carboxylate compound remained to give bands at 1588 and 1394 cm^{-1} and a 1643-cm^{-1} band was also detected, which is attributed to trace amounts of water [27].

3.3. *C_4H_6 and CO adsorption on unpromoted Ag*

To elucidate the nature of butadiene adsorption sites, the interaction of BD with a CO-covered Ag surface was studied. CO was introduced at 300 K to a sample of Ag/α-Al_2O_3 after reduction at 673 K, the cell was purged, and the spectrum A in Fig. 13 was taken. The catalyst was then exposed



(a)

(b)

Fig. 12. DRIFT spectra of BD adsorbed in the presence of O_2 on CsCl (994) at 473 K after a I-LT pretreatment; (a) during exposure to 68 Torr BD and 136 Torr O_2 (gas-phase BD spectrum subtracted); (b) after a 30-min purge.

to BD for 30 min and purged, and spectrum B was taken. Bands appeared in the $\nu(CH_x)$ region at 2974, 2942, and 2882 cm^{-1} which were similar to those obtained for clean Ag (although weaker), and bands were retained at 2018, 1927, and 915 cm^{-1} after purging. The interferogram taken just before exposure to CO was used also as a background for spectrum B in Fig. 13. The residual 1927-cm^{-1} band might suggest that the electronic effects due to π-donation of 1,3-butadiene caused a 30-cm^{-1} shift in ν(CO), which is indirect evidence for the presence of π-bonded species on the Ag catalysts. When spectrum B was subtracted from spectrum A, negative bands were observed in the 2035–1950 cm^{-1} spectral region, as shown by spectrum C in Fig. 13, which shows that much of the adsorbed CO was displaced by BD adsorption on this Ag surface and that CO and BD compete for the same adsorption sites. After reduction at 473 K, the BD uptake at 300 K on this Ag/α-Al_2O_3 was 0.2 µmol/g [26], while the CO uptake at 300 K was 0.15 µmol/g. This probably represents adsorption only on Ag surface atoms with low coordination numbers [27].

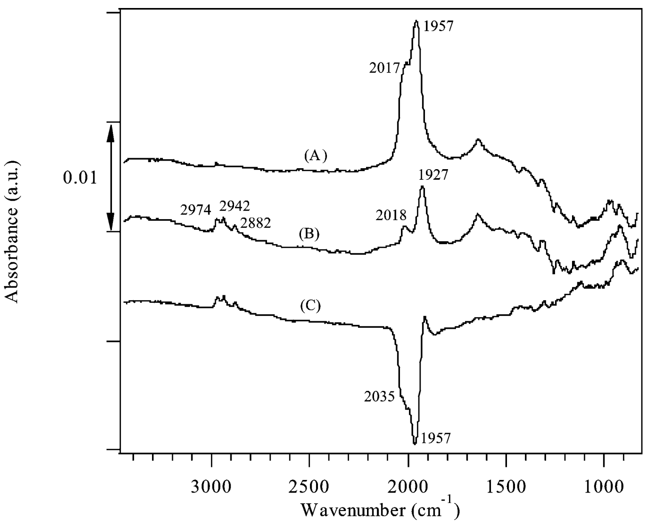


Fig. 13. DRIFT spectra after BD adsorption at 300 K on a CO-covered sample of UNP-II following a I-HT pretreatment; (A) after a 30-min purge following exposure to 76 Torr CO for 30 min at 300 K; (B) after spectrum A 68 Torr BD was introduced for 30 min followed by 30 min purge; (C) spectrum B subtracted from spectrum A.

4. Discussion

The adsorption of normal and D_6-labeled 1,3-butadiene on either reduced or O-covered Ag/α-Al_2O_3 catalysts at 300 and 473 K was investigated utilizing DRIFTS to gain insight about the chemistry associated with BD chemisorption on Ag surfaces. Such information is relevant to the mechanism involved in the catalytic epoxidation of this molecule to epoxybutene. The structure of 1,3-butadiene adsorbed on Ag has been previously studied. Osaka et al. used infrared-absorption reflection spectroscopy to conclude the following about BD adsorption on Ag (111) at low temperatures:

(a) BD occupies terrace sites at low coverages;
(b) BD adsorbs on kink and step sites as the coverage increases;
(c) monolayer coverage can occur; and
(d) multilayers form with an ordered state [17].

These authors reported that on Ag (111) the adsorbate lies parallel to the surface at 30 K, but at 90 K the molecular plane tilts with the C=C bonds remaining parallel to the surface. Coulman et al. used near-edge X-ray absorption fine structure spectroscopy (NEXAFS) and reported that BD chemisorbs with its σ_h plane parallel to the surface [50], similar to ethylene adsorption on a Ag (110) surface [51]. They found that the extent of chemical bonding between the BD and the surface is too weak to produce bond rehybridization. By employing surface-enhanced Raman spectroscopy and using ab initio molecular orbital frequency calculations, Itoh and co-workers showed that BD adsorption below 120 K on evaporated Ag films gave rise to one absorption feature in the C=C-stretching region at 1636 cm^{-1}, which was ascribed to BD adsorbed via one of the C=C bonds coordinated to a positively charged Ag site, whereas at 180 K this band shifted to 1631–1625 cm^{-1} and another band at 1606 cm^{-1} formed, which was associated with BD coordinated through both C=C bonds at positively charged sites [18–20]. Using extended Hückel theory, Schiøtt and Jørgensen probed the interaction between BD and atomically adsorbed oxygen on Ag (110) and reported that the interaction of only one of the terminal carbons of BD with surface oxygen was favored [22]. Their calculations indicated that when BD adsorbs on oxygen-covered Ag, the intermediate loses a considerable amount of its double-bond character and the C_2–C_3 overlap population increases, indicating this latter band increases its double-bond characteristics. Similarly, tight binding calculations performed by Baetzold on BD chemisorption on fcc (111) metal faces showed that the middle C–C bond gains double-bond character, while the terminal C–C bonds weaken; however, the nature of the metal was not taken into account [52]. Monnier has also suggested that the interaction of butadiene with a Ag surface is through a single localized C=C double bond [5].

In the current study, a 1,2-BD-type species was dominant on the surface of the unpromoted Ag/α-Al_2O_3 catalyst at 300 K. This is consistent with the proposal that, due to its strong interaction the Ag sites, one terminal C=C bond loses double-bond character while the middle C–C bond gains double-bond character. Moreover, the bands at 2977, 2938, and 2882 cm^{-1}, which are ascribable to CH_3/CH_2-stretching modes, were indicative of the formation of sp^3-hybridized C atoms, as reported earlier for BD adsorption on Rh [53,54]. Vapor-phase 1,2-BD gave rise to a band at 1957 cm^{-1} due to the C=C-stretching mode [34], whereas a band at 2017 cm^{-1} occurred on Ag/α-Al_2O_3 reduced at 673 K from whose surface oxygen was removed. Isotopic studies revealed that this adsorbed species interacts with Ag atoms but not with surface oxygen.

4.1. *Adsorption of C_4H_6 and C_4D_6 on promoted Ag catalysts*

Studies using isotopically labeled adsorbates provided valuable information to help identify surface species. Bands were observed between 1400 and 1600 cm^{-1}, which can represent ν(C=O), δ(CH), and ν(C=C) modes in complexes with weakened C=C bond vibrations in the oxygen–hydrocarbon system. For deuterium-labeled hydrocarbons, an isotope shift of 300–400 cm^{-1} should occur in the CH-bending vibrations [34]. For complexes with weakened C=C bonds, the isotope shift is 90–150 cm^{-1} for deuterium-labeled olefins [55,56], while the C=O-stretching vibration is not significantly shifted, i.e., it is only about 10–20 cm^{-1} [34,49]. If the adsorbed species have a carboxylate structure, the shift is expected to be about 20–30 cm^{-1} with ^{18}O present [49].

On the Ag catalyst promoted only with Cs, weak bands ascribable to a 1,2-BD-type species were observed after LT pretreatments, as shown in Fig. 5, and a dominant band appeared at 1576 cm^{-1} which is attributed to the C=C stretching of a surface carbonaceous species, based on the isotope studies. After a HT reduction at 673 K, however, the dominant band on this catalyst was at 1473 cm^{-1} and it is attributed to a ν(C=C) stretching mode in a dehydrogenated surface species containing a weakened C=C bond. All these results suggest that Cs facilitates additional C–C and C–H bond breaking under our experimental conditions. On O-covered CsN (1175) a band appeared at 1577 cm^{-1} due to the C=C-stretching mode in a carbonaceous species. This implies the formation of carbonaceous species on the surface due to AgO-assisted C–H cleavage, as explained later, because on samples reduced at 673 K, Cs suboxides are the only source of residual oxygen [27] and this 1572-cm^{-1} band was not observed. With this Cs-promoted Ag/α-Al_2O_3 catalyst after a II-HT treatment, a 1972-cm^{-1} band was also detected, but no bands were discernable in the CH_x-stretching region.

Studies with BDD6 indicated that the 1972-cm^{-1} band was due to a C=C-stretching mode in a dehydrogenated 1,2-BD-type species. The composition of this surface species was clarified after BD adsorption on an ^{18}O-covered CsN (1175) catalyst because the band at 1972 cm^{-1} shifted to 1952 cm^{-1} and a band at 1994 cm^{-1}, which was not detected with the ^{16}O-covered sample, was observed along with bands in the CH_x-stretching region, as shown in spectrum D in Fig. 5. To better understand BD adsorption, information about the nature of the adsorption site is useful. As discussed elsewhere [27], oxygen appears to induce formation of $AgCs_xO_y$ surface sites, and more of these composite sites were formed on this Cs-promoted Ag/α-Al_2O_3 catalyst during O_2 adsorption following reduction at 673 K than after reduction at 473 K [27]. This implies that the HT pretreatment facilitates the formation of these composite surface sites. Jin et al. have studied Pd–Ag catalysts and have concluded that a higher temperature pretreatment in H_2 enhances the mobility of surface silver atoms, which were added as a promoter, and leads to surface structures in which domains of Pd are separated by islands of Ag [57]. Similarly, it is possible that HT reduction at 673 K causes redistribution of Cs atoms, and $AgCs_xO_y$ sites can be formed when O_2 is introduced at 443 K. Monnier has shown that a Cs promoter interacts more effectively with Ag if deposited before reduction of the Ag salt (the reduction temperature, however, was not given) because the butadiene conversions were considerably higher after the latter procedure [9].

For Cs-promoted Ag/α-Al_2O_3 after $^{18}O_2$ adsorption, the band at 1994 cm^{-1} was similar to that obtained with unpromoted Ag/α-Al_2O_3, which implies that the 1,2-BD-type species was formed from BD adsorption on Ag sites only (Fig. 5). Moreover, the band at 1994 cm^{-1} did not red-shift, indicating that this surface species did not contain oxygen and involved only Ag atoms, presumably positively charged. On the other hand, the band at 1972 cm^{-1} red-shifted to 1952 cm^{-1}, thus indicating the 1,2-BD-type species was interacting with surface oxygen. The dissociative sticking probability for $^{16}O_2$ is 1.4 times the dissociative sticking probability of $^{18}O_2$, independent of coverage [58]; in addition, prior to BD adsorption on the ^{16}O-covered sample, 76 Torr O_2 in He was flowed continuously, whereas for BD adsorption on the ^{18}O-covered sample, 76 Torr $^{18}O_2$ was introduced under static conditions. Thus the coverage of ^{18}O could easily be lower than that of ^{16}O. BD adsorbed on unpromoted Ag/α-Al_2O_3 to give a 1,2-BD-type species, regardless of whether the surface was reduced or O-covered; therefore, the species giving the 1994-cm^{-1} band cannot be associated with a decrease in adsorbed O atoms associated only with Ag_s atoms. This suggests that this species might represent the first step for BD adsorption on CsN (1175). The second step would involve the binding of the 1,2-BD-type species to surface oxygen associated with both Ag and Cs atoms, as previously explained. Since the coverage of dissociatively adsorbed oxygen is lower for ^{18}O, not all of the 1,2-BD-type species can interact with surface oxygen via its other terminal C=C bond. Considering this, it is proposed that BD first adsorbs on Ag-only sites to give a 1,2-BD-type species with a terminal C=C=C bond structure and the other terminal C atom coordinates with ^{18}O at a $AgCs_xO_y$ site. We presume that BD can adsorb through both C=C bonds on CsN (1175) to form an oxa-metallacycle, i.e., a cyclic structure with bonding to a metal surface through both ends. For epoxidation reactions, especially with ethylene, oxa-metallacycle species have been considered an intermediate, although they have been proposed only on clean Ag [59–64]. However, Saravanan et al. performed density functional theory calculations for a cluster modeling the Ag (111) face to examine the effect of Cs on an oxametallacycle intermediate, and they showed that ethylene binds to an oxygen atom on this Ag cluster to form an –O–C_2H_4 species which is not an oxametallacycle, but with Cs present, an oxametallacycle intermediate was formed [65]. It was suggested that Cs acts as an electron donor for oxametallacycle formation without being a part of the ring. Based on NEXAFS results, Medlin et al. proposed that when EpB is adsorbed on Ag (110), the double-bond character shifts to the middle C–C atoms due to a strong interaction between the terminal C atom and the surface, and the epoxide ring opens and bonds to a Ag atom to form an oxametallacycle [63]. As discussed elsewhere [47,66], there was no evidence for an oxametallacycle intermediate on either UNP-II or CsN (1175) after EpB adsorption. In this study, the oxametallacycle which is bonded to both Ag and $AgCs_xO_y$ sites would be an intermediate for EpB formation if it is not dehydrogenated.

Monnier studied the kinetics of BD partial oxidation to EpB and found that the pressure dependencies on both EpB and CO_2 exhibited transitions from fractional negative orders to negative first order, while the oxygen dependency was first order and that for BD was zero order until very low partial pressures of BD are reached. These results are consistent with a dual-site mechanism describing the BD epoxidation reaction [5]. Our findings are consistent with the proposal by Monnier that one site includes unpromoted Ag while the second site consists of Cs-promoted Ag, with the former serving as a site for butadiene adsorption and the latter site dissociatively adsorbing oxygen which reacts with adsorbed C_4H_6 to form EpB. The two steps associated with the two surface species formed by BD on an ^{18}O-covered Cs-promoted Ag catalyst, i.e., adsorption on a Ag-only site and adsorption involving both a Ag-only and a $AgCs_xO_y$ site, indicate that oxygen dissociation, which is diminished for $^{18}O_2$ compared to $^{16}O_2$, plays an important role in BD epoxidation. Monnier et al. have proposed that O_2 dissociation might be the rate-determining step in EpB formation [24]. On ^{18}O-covered CsN (1175), unlike the ^{16}O-covered sample, bands were observed in the CH_x-stretching region (Fig. 5) which suggest that oxygen plays a role in C–H bond breaking. Shustorovich and Bell have shown using the BOC-MP method that predosed adsorbed O atoms at low coverage facilitate C–H bond cleavage on Ag [67]. Based on all these results, it can be argued that dissociatively adsorbed oxygen is altered by Cs as reported by Salazar et al. [68], and this oxygen may determine the reaction pathway on Cs-promoted Ag catalysts. These authors found that there is an optimum coverage of Cs which results in less C–H bond breaking and facilitates the reaction between atomic oxygen and hydrocarbon to give the partial oxidation product.

When BD was adsorbed on CsCl (994) at 300 K, the interaction between the BD and the surface was very weak, and only one weak band in the 1629–1606 cm^{-1} spectral region due to the C=C-stretching vibration was observed. This is consistent with an earlier study which found that the apparent heat of adsorption values for BD on the reduced and the O-covered CsCl (1155) catalyst were only 10 and 5 kcal/mol, respectively, whereas the respective values for UNP-II and CsN (1175) were much higher, i.e., 210 and 64 kcal/mol for UNP-II, and 130 and 19 kcal/mol for CsN (1175), respectively, [26]. Table 4 shows the proposed surface species on Ag catalysts after 1,3-BD adsorption at 300 K.

4.2. C_4H_6 adsorption on supported Ag catalysts under reaction conditions

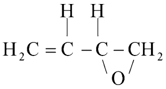
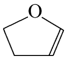
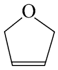
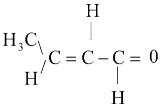
In the current study, the presence of Cs appears to provide a composite $AgCs_xO_y$ site which allows BD coordination with atomic oxygen, but this adsorbed state may lead to C–H bond breaking and preclude EpB formation. Earlier it was proposed that a dehydrogenated 1,2-BD-type species is formed on ^{16}O-covered CsN (1175) at 300 K; thus, EpB may not be formed when BD is adsorbed under reaction conditions, as discussed later. There are two pathways possible for the reaction between chemisorbed oxygen atoms and butadiene:

(i) activation of acidic C–H bonds by oxygen, and

Table 4
Proposed surface species on Ag catalysts after 1,3-BD adsorption at 300 K

Surface species	Bonds	ν (C=C=C)	ν (CH_3/CH_2/CH)	ν (C=C)	ν (C=O)	Observed
1,3-BD	C=C–C=C		3105, 3088, 3001, 2975	1596		
1,2-BD-type on Ag site	Cumulated C=C bond	1993–2017	2979, 2938, 2883	–	–	UNP-II
Partially dehydrogenated 1,2-BD-type interacting with surface oxygen	(C–C=C=C)	1972	2980(w), 2936(w)	–	–	II-HT-pretreated CsN (1175)
Carbonaceous species	Aromatic conjugated C=C bonds	–	–	1577–1607	–	LT and II–HT-pretreated UNP-II and CsN (1175)
Carbonaceous species	Olefinic (weakened C=C bond)	–	–	1473, 1404–1418	–	CsN (1175)
Crotonaldehyde	C–C=C–C=O	–	–	–	1658	LT- and II-HT pretreated UNP-II

Table 5
Gibbs free energies of reaction of butadiene with oxygen

	Compound	ΔG_{rxn} (473 K) (kcal/mol) $BD + 1/2O_2 \rightarrow C_4H_6O$
EpB		-12.5[a]
2,3-DHF		-36.3[a]
2,5-DHF		-41.0[b]
CROALD		-45.4[b]

EpB, 3,4-epoxy-1-butene; DHF, dihydrofuran; CROALD, crotonaldehyde.

[a] From Ref. [69].

[b] From Ref. [45].

(ii) oxygen addition to a C=C double bond, with 1,2-addition leading to EpB, the desired product, and 1,4 addition forming 2,5-dihydrofuran.

Madix and co-workers reported that BD adsorption on Ag (110) added oxygen to give 2,5-dihydrofuran as well as furan, maleic anhydride, 4-vinylcyclohexene, 2(5H)-furanone, carbon dioxide, and water [21]. As noted earlier, Schiøtt and Jørgensen used extended Hückel tight-binding calculations to show that the BD intermediate on Ag (110) binds through one of its C=C bonds and reacts with an oxygen atom to preferentially form 2,5-dihydrofuran rather than EpB [22]. Monnier has reported that the reaction between BD and atomic oxygen produces EpB on CsCl-promoted Ag/α-Al_2O_3 and the formation of 2,5-dihydrofuran proceeds by the isomerization of EpB [5,9]. In our study, no evidence for 2,5-dihydrofuran was obtained under reaction conditions; however, 2,5-dihydrofuran was formed on alumina after EpB adsorption at either 300 or 473 K [66], which is consistent with Monnier's results. Table 5 tabulates Gibbs free energy values for the reactions between BD and oxygen to give different C_4H_6O products. Thermodynamically, formation of 2,5-dihydrofuran is more favorable than formation of EpB; however, all the isomers of EpB are thermodynamically more favorable than EpB, which indicates that the selective reaction is kinetically controlled.

In this study, BD adsorption on alumina at 473 K in the presence of oxygen gave rise to bands assigned to crotonaldehyde and carbonaceous species. BDD6 adsorption provided evidence that BD dehydrogenates when it adsorbs on alumina, and BD exhibited similar adsorption behavior on unpromoted Ag/α-Al_2O_3 under reaction conditions in that crotonaldehyde and carbonaceous species were again observed in addition to a carboxylate compound. It is known that the activity of unpromoted Ag/α-Al_2O_3 is low [5]; thus any EpB formation may not be detected. There are other complications regarding the detection of EpB. First, during exposure to BD, the principal surface species is reversibly adsorbed BD, which precludes the detection of any trace amounts of vapor-phase EpB. Second, EpB is very reactive and it may quickly undergo different reaction pathways to give carbonaceous and carboxylate compounds as well as crotonaldehyde, 2,5-dihydrofuran, acrolein, and acetaldehyde, as discussed elsewhere [66]. Carboxylate groups are the dominant surface species remaining after BD adsorption on CsN (1175) under reaction conditions and a 30-min purge. As noted earlier, dehydrogenated 1,2-BD-type species were observed, even at 300 K, which would not favor the formation of EpB. Furthermore, the above-noted complications with EpB formation also exist with the Cs-promoted Ag catalyst. With the Cs-promoted catalyst no band assignable to crotonaldehyde was observed which implies either that Cs blocked sites on alumina or that the crotonaldehyde underwent further oxidation to give carboxylate groups on the surface and combustion products.

The highest EpB yield during BD epoxidation was achieved by the addition of 950 ppm CsCl to a Ag/α-Al_2O_3 catalyst [9]; however, in our study, no EpB was detected on a CsCl (994) sample under reaction conditions after a I-LT pretreatment. Part of the reason for this may be due to the complications noted in the previous paragraph, but the absence of a gas-phase, Cl-containing promoter in the feed may also have contributed to this inability to produce detectable amounts of EpB. The HT reduction at 673 K, which provides a better interaction between Cs and Ag, could not be used because it led to Cl removal from the catalyst [47].

5. Summary

The adsorption behavior of BD on supported, promoted Ag catalysts at 300 K and also under reaction conditions was examined using in situ DRIFTS. BD adsorbs reversibly on α-Al_2O_3 at 300 K but it interacts strongly at 300 K with Al_2O_3-supported Ag, whether reduced or covered with a monolayer of oxygen, through one of the localized C=C double bonds. This led to a decrease in the double-bond character of the terminal C=C bond while the middle C–C bond gained double-bond character, and the following rehybridization resulted in a surface species with characteristics resembling 1,2-BD. This interaction between the terminal C atom and the Ag surface was stronger on a reduced surface than on an O-covered surface. On reduced Ag/α-Al_2O_3, this 1,2-BD-type species predominated on the surface, whereas BD adsorption on an O-covered surface produced crotonaldehyde and carbonaceous species in addition to 1,2-BD-type species. The formation of carbonaceous species on the O-covered Ag catalyst suggests that additional C–H bond breaking can occur in the presence of adsorbed oxygen. BD adsorption on a Ag surface after CO chemisorption revealed that BD and CO compete for the same adsorption sites, which implies that BD adsorbs on Ag atoms with low coordination numbers.

After reduction at either 473 or 673 K, C–C and C–H bond breaking occurred following BD adsorption at 300 K on Cs-promoted Ag/α-Al_2O_3. This is attributed to an electronic effect of Cs which donates electrons to Ag and creates a stronger interaction with adsorbed species. On an O-covered, Cs-promoted Ag/α-Al_2O_3 catalyst after reduction at 673 K, a dehydrogenated 1,2-BD-type species was observed in addition to carbonaceous species because Cs redistribution occurred during the pretreatment to allow composite $AgCs_xO_y$ sites to be formed. Evidence indicated that BD adsorbs through both C=C bonds on a Cs-promoted Ag catalyst and oxametallacycle formation is suggested. The first interaction involves only Ag atoms similar to those on unpromoted Ag/α-Al_2O_3, while the second interaction is associated with the composite $AgCs_xO_y$ site. On a catalyst promoted with both Cs and Cl, BD adsorbed only weakly on the Ag surface at 300 K regardless of the presence of chemisorbed oxygen; i.e., adsorption on a surface reduced at 473 K or one subsequently covered with chemisorbed oxygen gave similar results.

Under reaction conditions at 473 K, BD dehydrogenated on alumina to give carbonaceous species. In contrast, carboxylate compounds were the principal species on either unpromoted or promoted Ag catalysts, which suggests that total oxidation was occurring. On both the pure alumina and the Ag/α-Al_2O_3 catalysts, crotonaldehyde was also observed.

References

[1] E.A. Carter, W.A. Goddard III, J. Catal. 112 (1988) 80.
[2] E.A. Carter, W.A. Goddard III, Surf. Sci. 209 (1989) 243.
[3] E. Shustorovich, Surf. Sci. 279 (1992) 355.
[4] J.G. Serafin, A.C. Liu, S.R. Seyedmonir, J. Mol. Catal. A 131 (1998) 157.
[5] J. Monnier, Stud. Surf. Sci. Catal. 110 (1997) 135.
[6] J.A. Dean, Lange's Handbook of Chemistry, McGraw-Hill, New York, 1999.
[7] J.R. Monnier, P.J. Muehlbauer, US patent No. 4,897,498, 1990.
[8] J.R. Monnier, P.J. Muehlbauer, US patent No. 5,145,968, 1992.
[9] J.R. Monnier, Appl. Catal. A 221 (2001) 73.
[10] S. Hawker, C. Mukoid, J.P.S. Badyal, R.M. Lambert, Surf. Sci. 219 (1989) L615.
[11] C. Mukoid, S. Hawker, J.P.S. Badyal, R.M. Lambert, Catal. Lett. 4 (1990) 57.
[12] J.T. Roberts, R.J. Madix, J. Am. Chem. Soc. 110 (1988) 8540.
[13] J.L. Stavinoha Jr., J.R. Monnier, D.M. Hitch, T.R. Nolen, G.L. Oltean, US patent No. 5,362,890, 1994.
[14] S.D. Barnicki, J.R. Monnier, US patent No. 6,011,163, 2000.
[15] Chem. Eng. News, August 21, 7 (1995).
[16] D. Denton, S. Falling, J. Monnier, J. Stavinoha, W. Watkins, Chim. Oggi 5 (1996) 17.
[17] N. Osaka, M. Akita, K. Itoh, J. Phys. Chem. B 102 (1998) 6817.
[18] K. Itoh, M. Tsukada, T. Koyama, Y. Kobayashi, J. Phys. Chem. 90 (1986) 5286.
[19] N. Osaka, M. Akita, S. Fujii, K. Itoh, J. Phys. Chem. 100 (1996) 17606.
[20] K. Itoh, M. Yaita, T. Hasegawa, S. Fujii, Y. Misono, J. Electron Spectrosc. Relat. Phenom. 54/55 (1990) 923.
[21] J.T. Roberts, A.J. Capote, R.J. Madix, J. Am. Chem. Soc. 113 (1991) 9849.
[22] B. Schiøtt, K.A. Jørgensen, J. Phys. Chem. 97 (1993) 10738.
[23] J.R. Monnier, G.W. Hartley, J. Catal. 203 (2001) 253.
[24] J.R. Monnier, J.W. Medlin, M.A. Barteau, J. Catal. 203 (2001) 362.
[25] J.W. Medlin, J.R. Monnier, M.A. Barteau, J. Catal. 204 (2001) 71.
[26] M.V. Badani, J.R. Monnier, M.A. Vannice, J. Catal. 206 (2002) 29.
[27] J. Müslehiddinoğlu, M.A. Vannice, J. Catal. 213 (2003) 305.
[28] C. Morterra, G. Magnacca, Catal. Today 27 (1996) 497.
[29] V. Ermini, E. Finocchio, S. Sechi, G. Busca, S. Rossini, Appl. Catal. A 190 (2000) 157.
[30] C. Morterra, G. Ghiotti, E. Garrone, F. Boccuzzi, J. Chem. Soc., Faraday Trans. 1 72 (1976) 2722.
[31] E. Borello, G.D. Gatta, B. Fubini, C. Morterra, G. Venturella, J. Catal. 35 (1974) 1.
[32] H. Knözinger, P. Ratnasamy, Catal. Rev.—Sci. Eng. 17 (1978) 31.
[33] W. Hertl, M.L. Hair, J. Phys. Chem. 72 (1968) 4676.
[34] L.M. Sverdlov, M.A. Kovner, E.P. Krainov, Vibrational Spectra of Polyatomic Molecules, Wiley, New York, 1974.
[35] http://www.webbook.nist.gov.
[36] A.A. Davydov, Infrared Spectroscopy of Adsorbed Species on the Surface of Transition Metal Oxides, Wiley, London, 1990.
[37] L.H. Little, Infrared Spectra of Adsorbed Species, Academic Press, London, 1966.
[38] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Wiley, New York, 1986.
[39] C. Morterra, M.J.D. Low, Spectrosc. Lett. 15 (1982) 689.
[40] D.G. Blackmond, J.G. Goodwin Jr., J. Catal. 78 (1982) 34.
[41] M.S. Akhter, A.R. Chughtai, D.M. Smith, Appl. Spectrosc. 39 (1985) 143.
[42] D.J. Wood, Mikrochim. Acta (1988) 167.

[43] C. Blanco, J.F. Ferreras, Spectrosc. Lett. 24 (1991) 827.

[44] T.V. Voskoboinikov, B. Coq, F. Fajula, R. Brown, G. McDougal, J. Luc Couturier, Micropor. Mesopor. Mater. 24 (1998) 89.

[45] J.V. Ibarra, C. Royo, A. Monzón, J. Santamara, Vib. Spectrosc. 9 (1995) 191.

[46] C.L. Yaws, Chemical Properties Handbook, McGraw-Hill, New York, 1999.

[47] J. Müslehiddinoğlu, PhD thesis, The Pennsylvania State University, 2002.

[48] J.C. Evans, J.K. Wilmhurst, H.J. Bernstein, Can. J. Chem. 34 (1956) 1139.

[49] S. Pinchas, I. Laulicht, Infrared Spectroscopy of Labelled Compounds, Academic Press, London, 1971.

[50] D. Coulman, J.L. Solomon, R.J. Madix, J. Stöhr, Surf. Sci. 257 (1991) 97.

[51] J.L. Solomon, R.J. Madix, J. Stöhr, J. Chem. Phys. 93 (1990) 8379.

[52] R.C. Baetzold, Langmuir 3 (1987) 189.

[53] P. Basu, J.T. Yates Jr., J. Phys. Chem. 93 (1989) 2028.

[54] P. Basu, J.T. Yates Jr., J. Phys. Chem. 93 (1989) 6110.

[55] D.A. Adams, J. Chatt, J. Chem. Soc. 7 (1962) 2821.

[56] C. Sourisseau, B. Pasquier, Can. J. Spectrosc. 18 (1973) 91.

[57] Y. Jin, A.K. Datye, E. Rightor, R. Gulotty, W. Waterman, M. Smith, M. Holbrook, J. Maj, J. Blackson, J. Catal. 203 (2001) 292.

[58] P.H.F. Reijnen, A. Raukema, U. van Slooten, A.W. Kleyn, Surf. Sci. 253 (1991) 24.

[59] G.S. Jones, M. Mavrivakis, M.A. Barteau, J.M. Vohs, J. Am. Chem. Soc. 120 (1998) 3196.

[60] J.W. Medlin, M. Mavrivakis, M.A. Barteau, J. Phys. Chem. B 103 (1999) 11169.

[61] G. Wu, M. Stacchiola, W.T. Kaltchev, W.T. Tysoe, Surf. Sci. 463 (2000) 81.

[62] D. Stacchiola, G. Wu, M. Kaltchev, W.T. Tysoe, J. Mol. Catal. A 167 (2001) 13.

[63] J.W. Medlin, M.A. Barteau, J.M. Vohs, J. Mol. Catal. A 163 (2000) 129.

[64] J.W. Medlin, A.B. Sherrill, J.G. Chen, M.A. Barteau, J. Phys. Chem. B 105 (2001) 3769.

[65] C. Saravanan, M.R. Salazar, J.D. Kress, A. Redondo, J. Phys. Chem. B 104 (2000) 8685.

[66] J. Müslehiddinoğlu, M.A Vannice, in preparation.

[67] E. Shustorovich, Surf. Sci. 268 (1992) 397.

[68] M.R. Salazar, J.D. Kress, A. Redondo, Catal. Lett. 64 (2000) 107.

[69] J.R. Monnier, private communication.