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In situ FTIR study of the adsorption and reaction of 2′-hydroxyacetophenone and benzaldehyde on MgO

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Abstract

The adsorption and reaction of 2′-hydroxyacetophenone and benzaldehyde on MgO were investigated via in situ FTIR spectroscopy in an attempt to gain a better understanding of the Claisen–Schmidt condensation reaction between these two molecules catalyzed by MgO. The results indicate that 2′-hydroxyacetophenone adsorbs on MgO through abstraction of the phenolic hydrogen, forming a surface phenolate ion. Benzaldehyde adsorbs through its carbonyl bond and can be subsequently oxidized to form two different types of benzoate species. These benzoate species are inactive toward further reaction with 2′-hydroxyacetophenone and/or its surface derivatives and accumulate on the MgO surface with time on stream. In contrast, the 2′-hydroxyacetophenone-derived phenolate ion reacts with benzaldehyde, yielding an adsorbed chalcone-type product.

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1. Introduction

Fine chemicals and pharmaceuticals have traditionally been synthesized via homogeneous catalytic methods. The use of heterogeneous catalytic processes offers certain advantages, including easier separation and recovery of the products and catalysts and minimization of the generated waste [1,2]. The synthesis of flavanone represents an example of a traditionally homogeneously catalyzed process that has been demonstrated to proceed over heterogeneous catalysts as well [3–7]. This synthesis consists of the Claisen–Schmidt condensation reaction between benzaldehyde and 2′-hydroxyacetophenone, followed by isomerization of the 2′-hydroxychalcone intermediate to flavanone, as shown in Scheme 1.

The kinetics of this scheme over MgO catalysts have been studied recently in our group [3–5]. In this paper we report the results of in situ Fourier transform infrared (FTIR) studies aimed at exploring the reactant–catalyst interactions, in an effort to advance our understanding of the surface chemistry involved in the Claisen–Schmidt condensation step on MgO.

2. Experimental

FTIR spectra were collected with a Nicolet 740 spectrometer equipped with a MCT-B detector cooled by liquid nitrogen. A homemade flow cell was used for the in situ measurements. This cell has a path length of 10 cm, and both ends are “capped” by IR-transparent NaCl windows. Approximately 13 mg of the MgO catalyst (Aldrich, 99+% purity, SA = 65 m^2/g) were pressed into a self-supported disc approximately 1 cm in diameter. This disc was placed in a sample holder located at the center of the cell. The cell was heated externally, and the temperature was measured with a thermocouple placed in close proximity to the catalyst sample. Transmission spectra were collected in a single-beam mode with a resolution of 2 cm^{-1}.

Before each experiment, the catalyst was pretreated in flowing nitrogen at 160 °C for 2 h to remove any water or other impurities from its surface. Spectra of the clean catalyst surface were collected following this procedure at the adsorption temperature and were used thereafter as background. Adsorption

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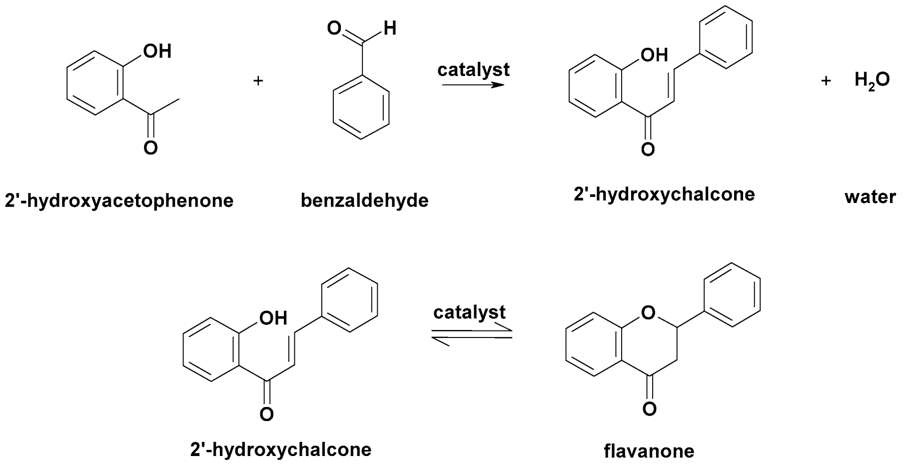
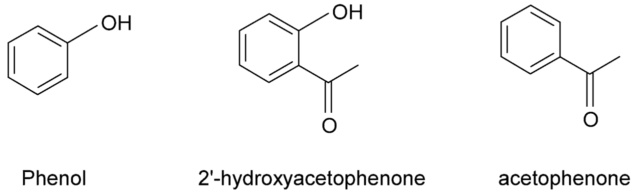


Scheme 1. Synthesis of flavanone via a two-step process.



Scheme 2. Structures of different molecules used in this study.

Table 1
Phenol band assignments

IR band (cm^{-1})	Assignment	Reference
Gas phase phenol		
1182, 1347	OH bending	[8–10]
1259	Combination of C–O stretching, C–H bending and C–C bending	[8–10]
1604, 1498, 1469	C=C stretching	[8–10]
1145, 1168	C–H bending	[8–10]
Adsorbed phenolate on MgO		
1283	C–O stretching	[10,12]
1252 (s)	C–H bending	[10]
1595, 1489, 1467	C=C stretching	
1149, 1165	C–H bending	

studies were conducted by exposing the catalyst to a stream of flowing nitrogen carrying a small concentration of the organic molecule of interest (i.e., 2′-hydroxyacetophenone, benzaldehyde, phenol, or acetophenone; the later two studied for band assignment purposes) obtained through passage of the nitrogen stream through a saturator. Spectra were collected at different time intervals until surface saturation was reached (i.e., spectral features were no longer changing as a function of time). Following saturation, the catalyst was subjected to a temperature ramp (rate of approximately 2 K/min) and/or exposed to the second reactant, as indicated in the discussion that follows.

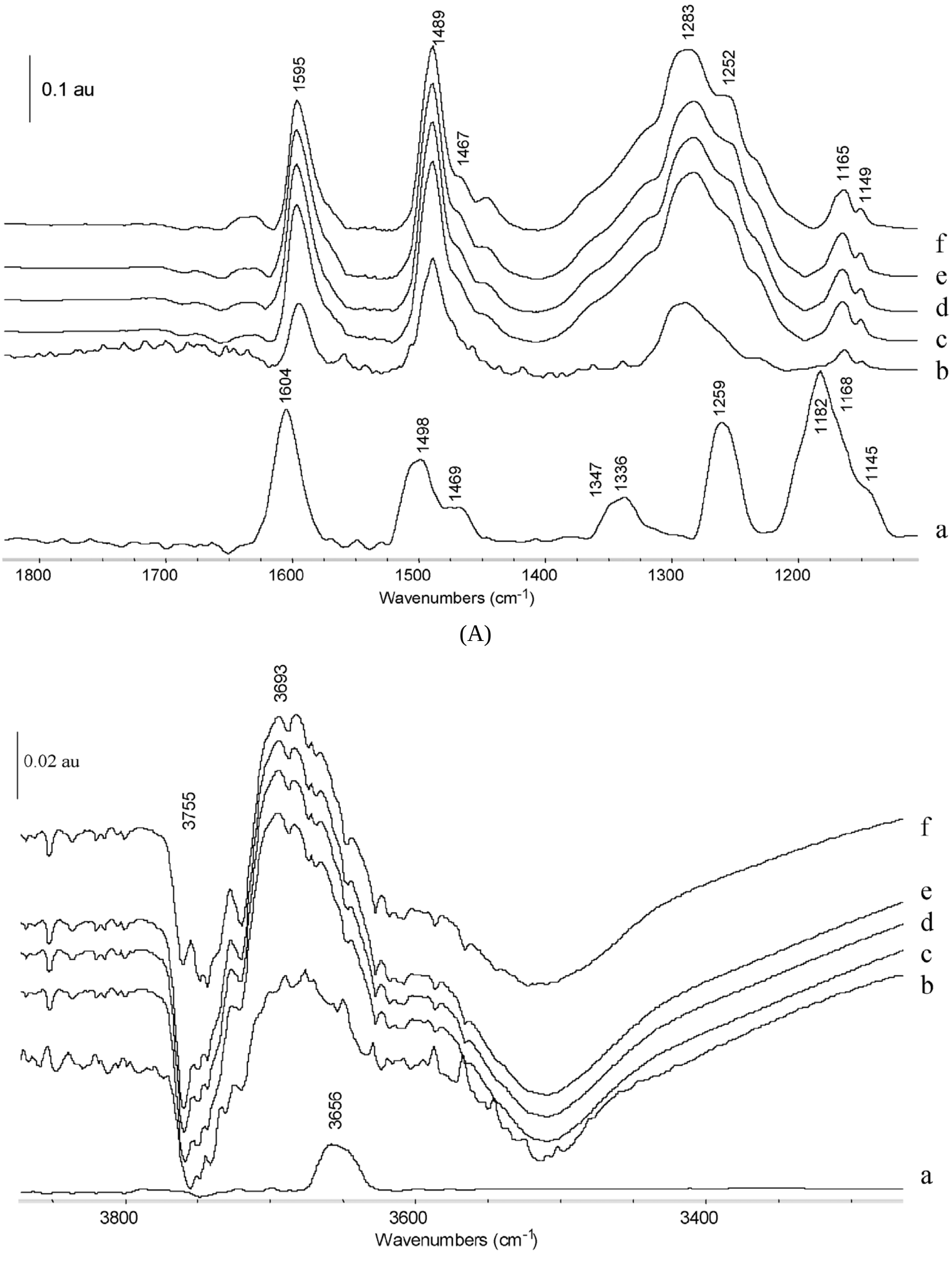
3. Results and discussion

In an attempt to deconvolute the spectra of adsorbed 2′-hydroxyacetophenone, we first examined the adsorption of phenol and acetophenone on MgO. As shown in Scheme 2, each of these molecules contains one of the functional groups present in 2′-hydroxyacetophenone and, in principle, should yield simpler spectra that will be used for band assignments in the more complex 2′-hydroxyacetophenone spectra.

3.1. *Adsorption of phenol*

Spectra of MgO collected during the adsorption of phenol at 160 °C are shown in Fig. 1. A summary of the bands observed and their assignments is shown in Table 1. The OH bending vibrations of phenols are known to be coupled with C–C stretching and C–H bending vibrations, and hence are involved in several bands. However, the bands at 1182 and 1347 cm^{-1} in the spectrum of gas-phase phenol can be uniquely assigned to OH bending vibrations [8–10]. These two bands are not present in the spectra of the adsorbed phenol in Fig. 1A, suggesting that the adsorption of phenol on MgO proceeds through the hydroxyl group, in agreement with previous reports on different metal oxides [10–14].

A strong feature at 1259 cm^{-1} in the spectrum of gas-phase phenol can be assigned to a combination of C–O stretching, C–H bending, and C–C bending vibrations [8–10]. The spectra of adsorbed phenol contain a broad band at 1283 cm^{-1} with a shoulder at 1252 cm^{-1}, indicating a shift and splitting of the 1259 cm^{-1} band during adsorption. Bandara et al. [10] assigned a broad band at 1295 cm^{-1} to the C–O stretching vibration of chlorophenol adsorbed on iron oxide, whereas Miyata et al. [12] assigned bands at 1280 and 1210 cm^{-1} to the C–O stretching vibrations of phenol adsorbed on TiO_2 and V_2O_5, respectively. These results indicate that the frequency of the C–O stretching vibration of the phenol shifts during adsorption and this shift depends on the adsorbent. Hence in our study the band at 1283 cm^{-1} can be assigned to this vibration. Furthermore, the shoulder at 1252 cm^{-1} can be assigned to a C–H bending vibration [10]. The splitting of the 1259 cm^{-1} gas-phase band during adsorption can be attributed to the disturbance of the combination of the several vibrational modes contributing to this band in the gas-phase spectrum, caused by the MgO surface.



(A)

(B)

Fig. 1. In situ FTIR spectra of MgO exposed to phenol at 160 °C for (b) 1, (c) 10, (d) 20 and (e) 30 min, and (f) flushing of (e) with N_2 at 160 °C for 30 min. For comparison, the gas phase spectrum of phenol is also shown in (a). (A) 1100–1900 cm^{-1} region; (B) 3200–3900 cm^{-1} region.

Finally, the bands at 1595, 1489, and 1467 cm^{-1} in the spectra of Fig. 1A can be assigned to C=C stretching vibrations, whereas the bands at 1165 and 1149 cm^{-1} can be assigned to C–H bending vibrations [8–10]. The presence of these bands suggests that the aromatic ring remains intact during adsorption. Their slight shift from their corresponding positions in the spectrum of the gas-phase phenol can be attributed to changes in the electron distribution and symmetry of the aromatic ring during the adsorption process. Similarly, the weak bands at 1336 cm^{-1} in the spectrum of gas-phase phenol and at 1321 and 1367 cm^{-1} in the spectra of adsorbed phenol probably represent coupled C–C stretching and C–H bending vibrations [8]. Exposure of the adsorbed surface phenolate species formed to nitrogen for 30 min (Fig. 1A; spectrum f) did not result in any significant changes, indicating that this species is strongly bound on the MgO surface.

In the hydroxyl region the spectrum of gas-phase phenol (Fig. 1B; spectrum a) exhibits a well-defined band at 3656 cm^{-1}, which has been assigned to the OH stretching vibration of this molecule [8,9]. Following adsorption onto MgO, this band disappears and a new broader band centered at approximately 3693 cm^{-1} is observed (Fig. 1B; spectra b–f). The spectra of adsorbed phenol also contain a negative feature at 3755 cm^{-1}, indicating that some of the “free” (i.e., oxygen

Table 2
Acetophenone band assignments

IR band (cm^{-1})	Assignment	Reference
Acetophenone in KBr		
1685	C=O stretching	[8,18]
1360, 1426	CH_3 bending	[8,18]
1266	Mixed mode containing phenyl–$COCH_3$ and CO–CH_3 stretching	[8]
1598, 1581, 1449	Aromatic ring vibrations	[8,18]
1180, 1158	C–C stretching and C–H bending associated with the aromatic ring	[8,18]
Adsorbed acetophenone on MgO		
1678, 1649	Weakened C=O bond (Scheme 3)	[19]
1364, 1426	CH_3 bending	
1266	Mixed mode containing phenyl–$COCH_3$ and CO–CH_3 stretching	
1328	CC bond in a carbanion	[20]
1596	CO bond in a carbanion and aromatic ring vibrations	[20]
1560, 1596, 1449	Aromatic ring vibrations	
1180, 1158	C–C stretching and C–H bending associated with the aromatic ring	
1413	Methylene scissoring of the –CH_2–CO– group	[22]
1227	CH_2 group	[23]

atom bound to only one cation) surface hydroxyl groups of MgO (with a previously assigned OH stretching vibration in the 3745–3760 cm^{-1} region [15,16]) are eliminated during the adsorption step. A similar behavior was previously observed during the adsorption of methylbutynol on MgO and was attributed to the reaction of the OH group of the alcohol with the MgO surface [15,17]. More specifically, the dissociative adsorption of the alcohol can result in the formation of new hydrogen-bonded surface hydroxyl groups with the characteristic band at 3693 cm^{-1}. Alternatively, reaction of the alcohol hydroxyl group with the free surface hydroxyls (negative band at 3755 cm^{-1}) can also lead to the formation of a surface alcoholate species and water removal from the MgO surface. In our case, these results are consistent with those discussed previously for the low-wavenumber region, indicating that the adsorption of phenol on MgO proceeds through the hydroxyl group. The broadening of the 3693 cm^{-1} band and the presence of a lower-wavenumber shoulder at approximately 3610 cm^{-1} further suggest that some of the new surface hydroxyls formed may interact with the aromatic ring of the adsorbed phenolate species.

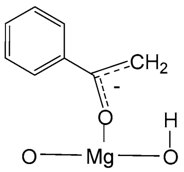
3.2. Adsorption of acetophenone

Spectra of MgO collected during the adsorption of acetophenone at 160 °C are shown in Fig. 2. A summary of the bands observed and their assignments is given in Table 2. The spectrum of acetophenone in KBr (Fig. 2A; spectrum a) contains a strong band at 1685 cm^{-1} characteristic of the C=O bond of this molecule [8,18]. During adsorption, this band splits to two new bands and shifts to lower wavenumbers (i.e., 1678 and 1649 cm^{-1}), indicating a weakening of the carbonyl bond due to the interaction with the catalyst surface. The presence of two bands in this region indicates that two slightly different surface species are formed. A similar behavior was observed during the adsorption of benzaldehyde on V_2O_5/TiO_2 by van Hengstum et al. [19]. In this case the formation of two slightly different coordinatively bonded aldehydes was proposed, with the aldehydic H still attached to the molecule and the C=O bond weakened. These two species react further at higher temperatures, resulting in the complete breakage of the C=O bond and to the formation of a surface benzoate species, as we describe in a later section.

The adsorption of acetophenone is comparable to the adsorption of benzaldehyde, and it is reasonable to assume that two similar species are also formed during the adsorption of acetophenone on MgO. However, at 160 °C the intensities of these bands decrease significantly following exposure to nitrogen (Fig. 2A; spectrum e), suggesting that the corresponding species are only weakly adsorbed on the surface.

A strong band at 1360 cm^{-1}, together with a shoulder at 1426 cm^{-1} in the spectrum of acetophenone in KBr, can be assigned to the symmetric and asymmetric CH_3 bending vibrations, respectively [8,18]. Both bands are present in the spectrum of adsorbed acetophenone on MgO, but their intensity decreases significantly under desorption conditions (i.e., exposure of the adsorbed acetophenone to nitrogen). This behavior suggests that only weakly adsorbed acetophenone species contain a CH_3 group. Furthermore, a band at 1266 cm^{-1} exhibits similar behavior. This band has been assigned to a mixed mode containing phenyl–$COCH_3$ and CO–CH_3 stretching character [8], and thus its behavior is once again consistent with the presence of a CH_3 group in a weakly adsorbed acetophenone species.

A strong band at 1328 cm^{-1} appears during the adsorption of acetophenone and is stable under desorption conditions. A similar band has been previously assigned to a $\text{C}\overset{\cdots}{-}\text{C}$ vibration in a $\text{O}\overset{\cdots}{-}\text{C}\overset{\cdots}{-}\text{CH}_2$ carbanion formed during the adsorption of acetophenone on $Ba(OH)_2$ [20]. In the current study, the 1328 cm^{-1} band can be assigned to a similar $\text{C}\overset{\cdots}{-}\text{C}$ vibration, emanating from a surface enolate anion formed following abstraction of a proton from the CH_3 group of acetophenone. This species is strongly adsorbed on the MgO surface, as indicated by the constant intensity of the 1328 cm^{-1} band under desorption conditions. The essential elimination of the CH_3 bands during desorption (as discussed in the previous paragraph) further supports such an assignment. Furthermore, the observed decrease in the intensity of the C=O stretching vibrations under desorption conditions suggests that the nature of the carbonyl bond in the enolate anion has been modified, leading us to suggest that the negative charge is conjugated with the C=O bond. Hence, the formation of the strongly adsorbed surface species shown in Scheme 3 is proposed.



Scheme 3. Adsorbed enolate anion formed upon exposure of MgO to acetophenone.

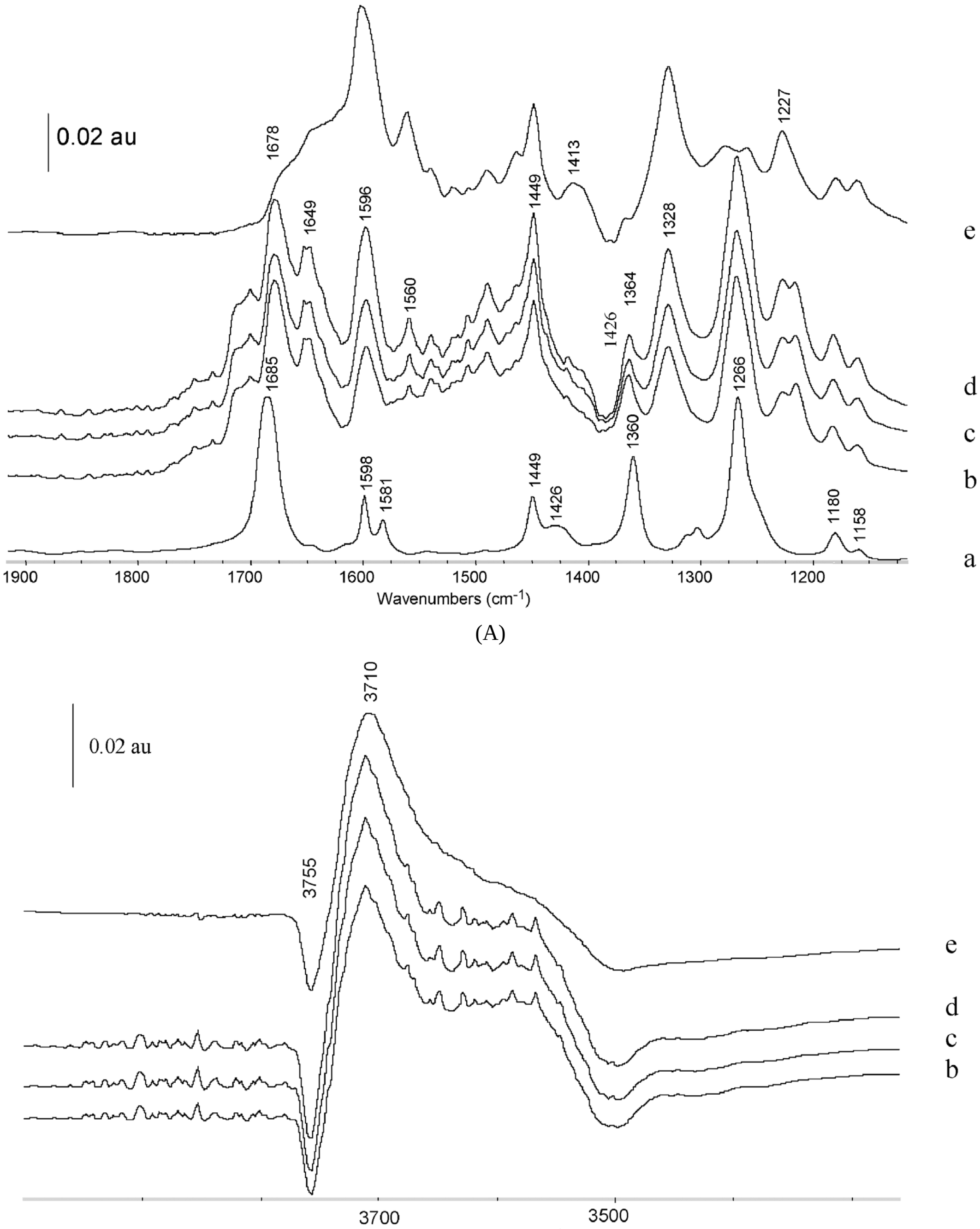


Fig. 2. In situ FTIR spectra of MgO exposed to acetophenone at 160 °C for (b) 10 min, (c) 20 min, (d) 30 min, and (e) flushing of (d) with N_2 for 30 min. For comparison, the spectrum of acetophenone in KBr is shown in (a). (A) 1100–1900 cm^{-1} region; (B) 3200–3900 cm^{-1} region.

Aguilera et al. [20] proposed the formation of a similar surface species during the adsorption of acetophenone on $Ba(OH)_2$. However, in their case the negative charge was proposed to be practically unconjugated with the $C{=}O$ bond, consistent with the presence of a band at 1680 cm^{-1} in the spectra of adsorbed acetophenone. In contrast, the same authors reported that the $C{=}O$ bond of alkyl ketones was disturbed during adsorption on $Ba(OH)_2$, and two new bands were observed at 1320 cm^{-1} (corresponding to the $C\overset{\cdots}{-}C$ bond in a $O\overset{\cdots}{-}C\overset{\cdots}{-}CH_2$ carbanion) and 1590 cm^{-1} (corresponding to the $O\overset{\cdots}{-}C$ bond in a $O\overset{\cdots}{-}C\overset{\cdots}{-}CH_2$ carbanion). Consistent with these results, in addition to the 1328 cm^{-1} band, a band is also present at 1596 cm^{-1} in the spectra of adsorbed acetophenone (Fig. 2A). This band probably contains some contribution from the aromatic ring vibration (as discussed in the next paragraph). However, the substantial increase in its intensity in the spectra of adsorbed acetophenone (as compared to the 1598 cm^{-1} band in the spectrum of acetophenone in KBr) also suggests a contribution from an adsorbed species, and in particular the $O\overset{\cdots}{-}C$ vibration of the enolate anion. Finally, the formation of the enolate anion shown in Scheme 3 is also consistent with the results of Diez et al. [21], who studied the adsorption and reaction of 2-propanol on MgO. This group proposed that propanol adsorption proceeds through the abstraction of the most acidic hydrogen, which in the case of the acetophenone would be one of the hydrogens of the CH_3 group. They also proposed that the adsorbed species is bound through the oxygen on a Mg atom, whereas the abstracted H is attached to an adjacent oxygen atom.

Three bands at 1596, 1560, and 1449 cm^{-1} are observed during the adsorption of acetophenone on MgO. Similar bands are also present at 1598, 1581, and 1449 cm^{-1} in the spectrum of acetophenone in KBr. These bands can be assigned to ring vibrations [8,18]. Their presence in the spectra of the adsorbed acetophenone indicates that the aromatic ring remains intact during adsorption. Additional bands at 1180 and 1158 cm^{-1}, once again observed in both the spectra of adsorbed acetophenone and the spectrum of acetophenone in KBr, can be also assigned to mixed modes of C–C stretching and C–H bending vibrations associated with the aromatic ring [8,18].

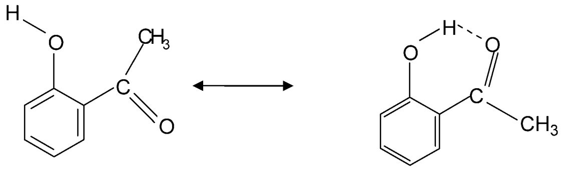
Some additional new bands appear in the spectra of adsorbed acetophenone and are stable under desorption conditions. A band at 1413 cm^{-1}, for example, can be assigned to the methylene scissoring vibration of the $–CH_2–CO–$ group [22]. Furthermore, the rocking, wagging, and twisting vibrational mode of such a CH_2 group occurs in the 1422–719 cm^{-1} region [23], and, consequently, a band at 1227 cm^{-1} can be probably assigned to such a mode. These two new bands are consistent with the formation of an adsorbed enolate ion, as proposed earlier in this paper.

Finally, the changes in the hydroxyl region of the spectra (Fig. 2B) are similar to those observed during the adsorption of phenol and consistent with the adsorption model depicted in Scheme 3 for acetophenone. More specifically, a new broad hydroxyl band centered at approximately 3710 cm^{-1} is formed during the adsorption of acetophenone. Bands in the 3700–3740 cm^{-1} region have been previously assigned to isolated multicoordinated hydroxyl groups (i.e., the O atom of the hydroxyl group is attached to more than one Mg atoms in the MgO surface) [16,24]. These surface hydroxyl groups are most likely created during the attachment to the surface of the hydrogen atom abstracted from the acetophenone molecule, as depicted in Scheme 3. The negative band at 3755 cm^{-1} indicates that some of the free surface hydroxyl groups of MgO may also react with such hydrogen atoms, leading to the removal of water from the surface.

3.3. *Adsorption of 2′-hydroxyacetophenone*

2′-Hydroxyacetophenone is known to exhibit strong intramolecular hydrogen bonding due to the presence of the hydroxyl and carbonyl groups in adjacent positions [8,25,26]. Hence, different conformers have been suggested for this molecule. Simple examples of the structure of 2′-hydroxyacetophenone with and without the intramolecular hydrogen bonding are shown in Scheme 4.

Additional structures involving hydrogen bonding have also been proposed by Palomar et al. [26], who reported that almost 100% of the 2′-hydroxyacetophenone molecules are internally hydrogen-bonded. Al-Rashid et al. [25] suggested that intramolecular hydrogen bonding is present at low concentrations in the vapor phase, whereas both intermolecular and intramolecular hydrogen bonding are present in the liquid phase, and attributed differences observed in the liquid- and gas-phase FTIR spectra of 2′-hydroxyacetophenone to such structural differences. Finally, results of theoretical studies indicate that several bond lengths of the 2′-hydroxyacetophenone molecule are changing upon intramolecular hydrogen bonding [26]. Consequently, due to the breakage of the intramolecular and intermolecular hydrogen bonding during the adsorption of 2′-hydroxyacetophenone on MgO, most of the infrared bands of the adsorbed molecule are expected to shift from the corresponding vapor phase positions because electron distribution and symmetry will change. Furthermore, significant discrepancies regarding the IR assignments of the pure component exist in the literature, due to the difficulty of distinguishing pure bond vibrations for this molecule [8,25,27].



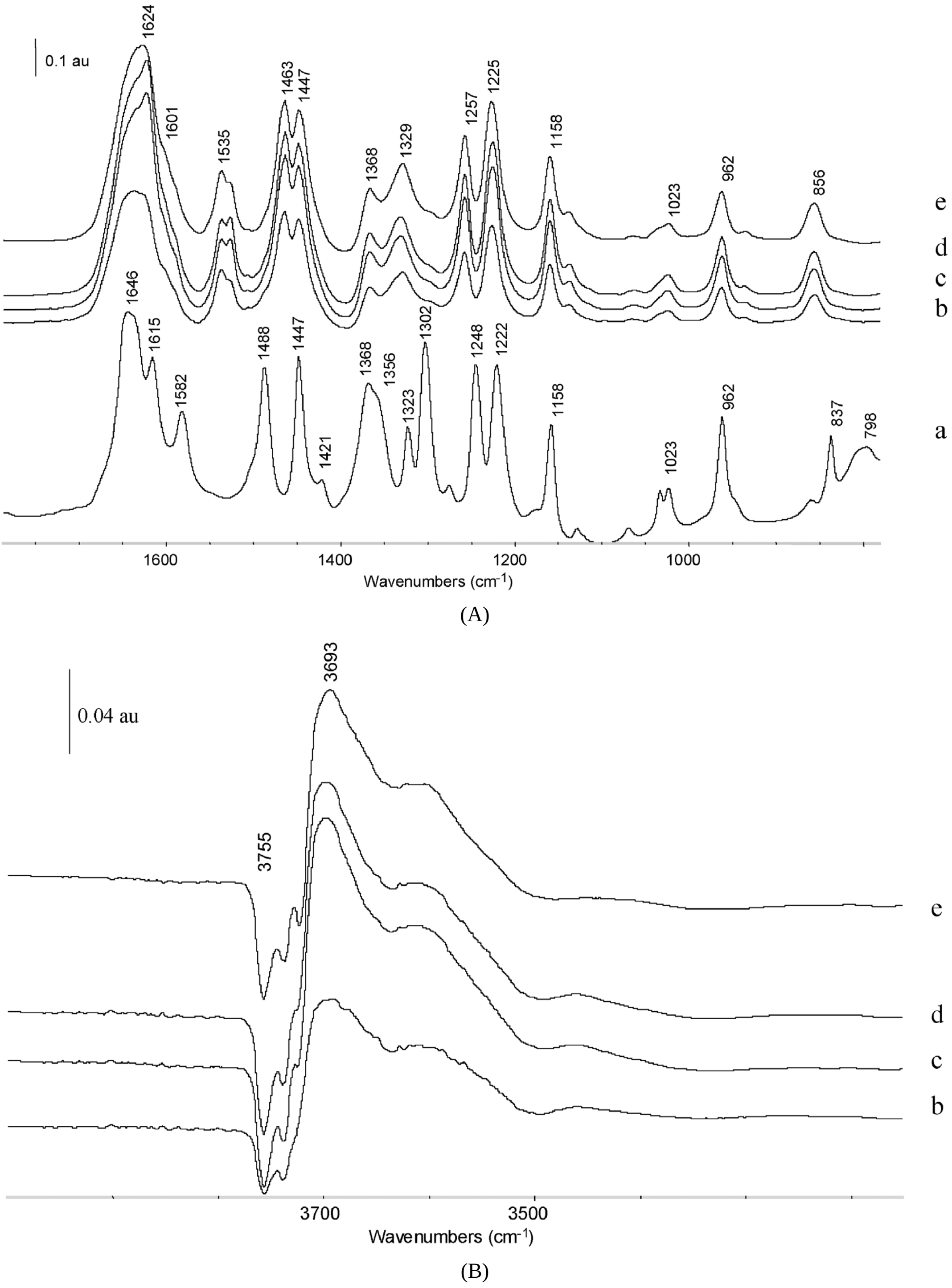
Non-hydrogen bonded 2′-hydroxyacetophenone

Intramolecularly hydrogen bonded 2′-hydroxyacetophenone

Scheme 4. 2′-Hydroxyacetophenone conformers.

Spectra of MgO collected during the adsorption of 2′-hydroxyacetophenone at 160 °C are shown in Fig. 3. The bands observed and their assignments are summarized in Table 3. The spectrum of liquid-phase 2′-hydroxyacetophenone (Fig. 3A; spectrum a) contains a strong band at 1646 cm^{-1}, which can be assigned to the C=O stretching vibration of the carbonyl group [8,25,27]. This band shifts to a lower wavenumber (1624 cm^{-1}) following adsorption, indicating a weakening of the corresponding bond, and hence, an interaction with the MgO surface. The new band is rather broad, suggesting the possible presence of two different surface species. A shift of the carbonyl bond was also observed during the adsorption of acetophenone on MgO (see Section 2), and the formation of two different surface species was proposed in that case as well. In contrast to the adsorption of acetophenone, however, the C=O band does not disappear from the spectrum of the adsorbed 2′-hydroxyacetophenone under desorption conditions (Fig. 3A; spectrum e), suggesting that in this case the carbonyl bond belongs to a strongly adsorbed surface species. This behavior implies differences in the mode of adsorption of acetophenone and 2′-hydroxyacetophenone on MgO.

Several bands in the 1300–1400 cm^{-1} region have been previously assigned to the OH stretching vibrations of 2′-hydroxyacetophenone. In particular, Palomar et al. [8] assigned a band at 1356 cm^{-1} to a pure OH in-plane bending vibration and a band at 1324 cm^{-1} to a mixed mode containing some OH bending character. Al-Rashid et al. [25] assigned bands at 1328 and 1360 cm^{-1} to the same vibration. These two groups



(A)

(B)

Fig. 3. In situ FTIR spectra of MgO exposed to 2′-hydroxyacetophenone at 160 °C for (b) 10, (c) 20 and (d) 30 min, and (e) flushing of (d) with N_2 at 160 °C for 30 min. For comparison, the spectrum of 2′-hydroxyacetophenone in the liquid phase is shown in (a). (A) 1100–1900 cm^{-1} region; (B) 3200–3900 cm^{-1} region.

have also assigned bands at 787 [8], 809, and 770 cm^{-1} [25] to OH out-of-plane bending vibrations. Based on these assignments, bands at 1356, 1323, and 798 cm^{-1} observed in the spectrum of liquid-phase 2′-hydroxyacetophenone (Fig. 3A; spectrum a) can be assigned to bending vibrations of the hydroxyl group. All of these bands disappear following adsorption of 2′-hydroxyacetophenone on MgO, suggesting an interaction with the MgO surface through abstraction of the phenolic hydrogen. This interaction can also be described in “acid–base” terms, given the acidic nature of the phenolic group and the basic nature of the MgO surface.

During the adsorption of phenol on MgO (see Section 1), the C–O stretching frequency was shifted to higher wavenumbers. Hence, a similar behavior is also expected in the case of 2′-hydroxyacetophenone. There are apparent discrepancies in the literature regarding the frequency of this C–O stretching vibration. Palomar et al. [8] assigned a strong band at 1305 cm^{-1} to a mixed mode containing mainly C–O stretching character, based on quantum chemical calculations and experimental data. In contrast, Al-Rashid et al. [25] assigned a band at 1224 cm^{-1} to the same vibration, whereas Gupta and Gupta [27] made a similar assignment to a band at 1230 cm^{-1}. In our case, the spectrum of liquid-phase 2′-hydroxyacetophenone (Fig. 3A; spectrum a) contains a strong band at 1302 cm^{-1} that disappears following adsorption of 2′-hydroxyacetophenone onto the MgO. Furthermore, a new band appears at 1329 cm^{-1}, which is believed to represent the same vibrations for the adsorbed 2′-hydroxyacetophenone species.

To further confirm this hypothesis, we conducted the adsorption of 2′-hydroxyacetophenone at different temperatures (i.e., 70, 110, and 160 °C); the spectra collected are shown in Fig. 4. The intensity of the band at 1302 cm^{-1} is very low even at 70 °C (Fig. 4; spectrum a), and the band essentially disappears with a further increase in temperature (Fig. 4; spectra b and c). At the same time, the new band at 1329 cm^{-1} grows in intensity with temperature and remains stable under desorption conditions (Fig. 3A; spectrum e and Fig. 4; spectrum d), in agreement with the results observed during the adsorption of phenol. All of these results indicate that a strongly held phenolate ion is formed on the MgO surface during the adsorption of 2′-hydroxyacetophenone.

In addition to the C=O (1624 cm^{-1}) and C–O (1329 cm^{-1}) bands of the proposed phenolate species, bands corresponding to a symmetric CH_3 bending vibration (1368 cm^{-1} [8,25]) and a CH_3 rocking vibration (962 cm^{-1} [8,25] and 1023 cm^{-1} [8]) are also observed in the spectra of the adsorbed 2′-hydroxyacetophenone and are stable under desorption conditions (Fig. 3A; spectrum e). This behavior indicates that the 2′-hydroxyacetophenone is strongly adsorbed on MgO through abstraction of the phenolic hydrogen and not through abstraction of hydrogen from the methyl group. The corresponding surface species is illustrated in Scheme 5. Such a structure is in agreement with the results of Diez et al. [21], who proposed that the abstraction of the most acidic H is the first step in the adsorption of propanol on MgO. Furthermore, the concentration of surface species is higher after the adsorption of phenol and 2′-hydroxyacetophenone than in the case of acetophenone, indicating that the adsorption proceeds faster through the phenolic group.

Table 3
2′-Hydroxyacetophenone band assignments

IR band (cm^{-1})	Assignment	Reference
Liquid phase 2′-hydroxyacetophenone		
1646	C=O stretching	[8,25,27]
798, 1323, 1356	O–H bending	[8,25]
1302	C–O stretching	[8,25,27]
1368	Symmetric CH_3 bending	[8,25]
962, 1023	CH_3 rocking	[8,25]
1447, 1488 1582, 1615	Aromatic ring vibrations	[8,18,28]
1158	C–H bending	[8,25]
837, 1248	Mixed mode related to the $COCH_3$ group	[8,25,27]
1222	Complex vibrational mode containing CH, CC, OH and ph–$COCH_3$ contributions	[8]
Adsorbed 2′-hydroxyacetophenone on MgO		
1624	C=O stretching	
1329	C–O stretching	
1368	Symmetric CH_3 bending	[8,25]
962, 1023	CH_3 rocking	[8,25]
1447, 1465 1532, 1601	Aromatic ring vibrations	
1158	C–H bending	[8,25]
856, 1257	Mixed mode related to the $COCH_3$ group	
1225	Complex vibrational mode containing CH, CC, OH and ph–$COCH_3$ contributions	[8]

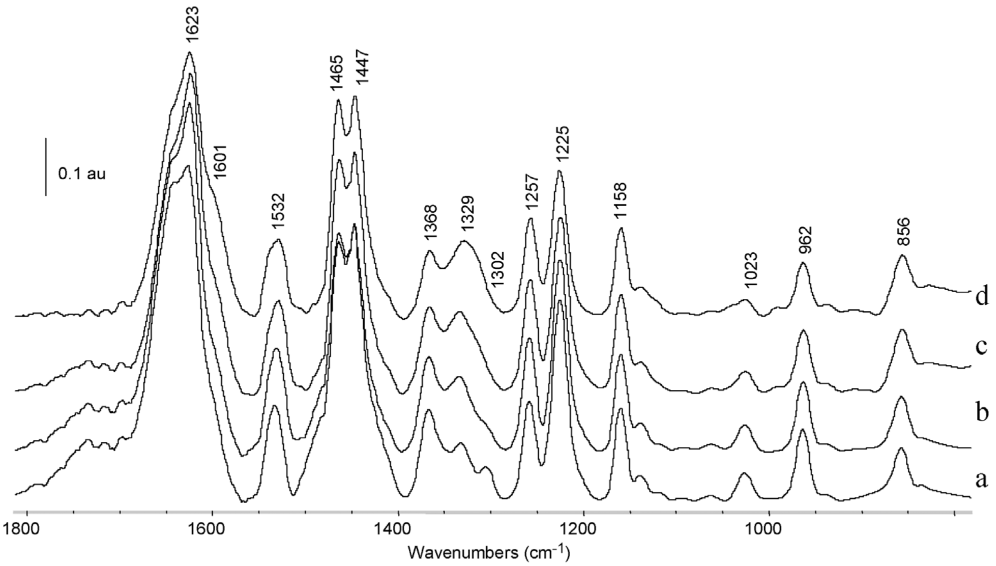
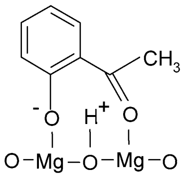


Fig. 4. In situ FTIR spectra of MgO exposed to 2′-hydroxyacetophenone for (a) 30 min at 70 °C, (b) 10 min at 110 °C, (c) 10 min at 160 °C and (d) flushing of (c) with N_2 for 30 min.



Scheme 5. Proposed structure for 2′-hydroxyacetophenone adsorbed on MgO.

Bands at 1615, 1582, 1488, and 1447 cm^{-1} in the spectrum of liquid-phase 2′-hydroxyacetophenone (Fig. 3; spectrum a) can be assigned to aromatic ring vibrations [8,18,28]. These bands are shifted to 1601 (sh), 1532, 1465, and 1447 cm^{-1}, respectively, after the adsorption of 2′-hydroxyacetophenone onto MgO (Fig. 3; spectra b–e). The presence of these ring vibrations after adsorption of 2′-hydroxyacetophenone suggests that aromaticity is not interrupted. The observed shifts can be attributed to subtle structural changes resulting from the breakage of the intramolecular hydrogen bonding during the adsorption. An additional band at 1158 cm^{-1} that remains unchanged during adsorption can be assigned to in-plane C–H bending vibrations [8,25].

Finally, some additional bands present in the spectra of Fig. 3 have been previously assigned to complex vibrations of the 2′-hydroxyacetophenone molecule. The assignments of these bands do not contribute to any further elucidation of the structure shown in Scheme 5. Nevertheless, for clarity and completion, we discuss them briefly. They include a band at 1248 cm^{-1} in the spectrum of liquid-phase 2′-hydroxyacetophenone, which shifts to 1257 cm^{-1} following adsorption. Similar bands have been previously assigned to a CO–C stretching vibration [25], a mixed mode containing mainly ring–$COCH_3$ and $CO–CH_3$ stretching vibrations [8], and a CCO bending vibration [27] of the liquid-phase molecule. Although, based on our data, it is not possible to determine the exact nature of the vibration, it is clear that this band belongs to a vibration of the $COCH_3$ group. Its small shift following adsorption could be rationalized in terms of the breakage of the intramolecular hydrogen bonding or the interaction of the C=O bond with the MgO surface, as indicated by the simultaneous shift of the carbonyl stretching frequency discussed earlier. A shift to higher wavenumbers was also observed for a band appearing at 837 cm^{-1} in the spectrum of liquid-phase 2′-hydroxyacetophenone to 856 cm^{-1} in the spectra of adsorbed 2′-hydroxyacetophenone. In the literature, this band has been assigned to several different modes, including C–C bending and stretching, ring–CO–CH_3 stretching, CO–CH_3 bending, C–O stretching [8], and a CH_3 rocking vibration [25]. Because a similar shift was observed for the band at 1248 cm^{-1}, which was assigned to the $COCH_3$ group, we propose that complex vibrations of the $COCH_3$ group are also responsible for the band at 837 cm^{-1}. Finally, a band appears at 1222 cm^{-1} in the spectrum of liquid-phase 2′-hydroxyacetophenone and remains almost unchanged (1225 cm^{-1}) following adsorption. Palomar et al. [8] assigned a band at 1218 cm^{-1} to a complex vibrational mode containing CH, CC, OH, and ph–$COCH_3$ vibrations of 2′-hydroxyacetophenone. A similar assignment can be used in our case for the 1222 cm^{-1} band.

Table 4
Benzaldehyde band assignments

IR band (cm^{-1})	Assignment	Reference
Gas phase benzaldehyde		
1723	C=O stretching	[8,9]
1383	Aldehydic C–H bond	[8,9]
1200	Mixed mode consisting of ring–COH stretching, aldehydic CH bending, and C=C stretching	[8,9]
1160, 1167, 1311	Aromatic ring vibrations and mixed modes of	[10,19,21]
1451, 1597	CH bending and C=C stretching	
Adsorbed benzaldehyde on MgO		
1625	C=O stretching of covalent carboxylate-type structure	[19,29]
1200	CH bending and C=C stretching	
1263	Ring–C stretching	[30]
1408, 1564	Bridging surface benzoate	[19,29,31,32]
1423	Surface benzoate	[19,32,33]
1160, 1175, 1306	Aromatic ring vibrations and mixed modes of	[10,19,21]
1447, 1601	CH bending and C=C stretching vibrations	

Changes in the hydroxyl region (Fig. 3B) are similar to those observed during the adsorption of phenol and acetophenone as discussed in detail earlier. Once again, the broad feature at 3693 cm^{-1}, characteristic of H-bonded surface hydroxyl groups, is present following 2′-hydroxyacetophenone adsorption on the MgO surface, consistent with the proposed model of dissociative adsorption through the phenolic group. Elimination of some of the free MgO surface hydroxyl groups is also observed (negative band at 3755 cm^{-1}), indicating in this case reaction with the phenolic group during 2′-hydroxyacetophenone adsorption and water removal from the surface.

3.4. *Adsorption of benzaldehyde*

Spectra of MgO collected during the adsorption of benzaldehyde at 160 °C are shown in Fig. 5. The bands observed and their assignments are summarized in Table 4. The spectrum of gas-phase benzaldehyde contains a very strong band at 1723 cm^{-1} that has been assigned to the stretching vibration of the C=O bond [8,9]. This band is also present in the spectra of adsorbed benzaldehyde (Fig. 5; spectra b–d). However, it quickly disappears when the MgO surface is exposed to a flow of nitrogen (Fig. 5; spectrum e), suggesting that it belongs to a weakly adsorbed/ physisorbed species. A new shoulder appears at 1625 cm^{-1} during the adsorption of benzaldehyde that can be assigned to the stretching vibration of a weakened C=O bond in a covalent carboxylate-type structure similar to the one shown in Scheme 6a [19,29]. This surface species can formed through the interaction of the carbonyl group of benzaldehyde with the MgO surface and abstraction of the aldehydic hydrogen.

Breakage of the aldehydic C–H bond is also supported by the disappearance of a band at 1383 cm^{-1} in the gas-phase benzaldehyde spectrum following adsorption. This band has been previously assigned to a bending vibration of the aldehydic C–H bond in the vapor phase [8,9]. Furthermore, an additional band at 1200 cm^{-1} in the spectrum of gas-phase benzaldehyde

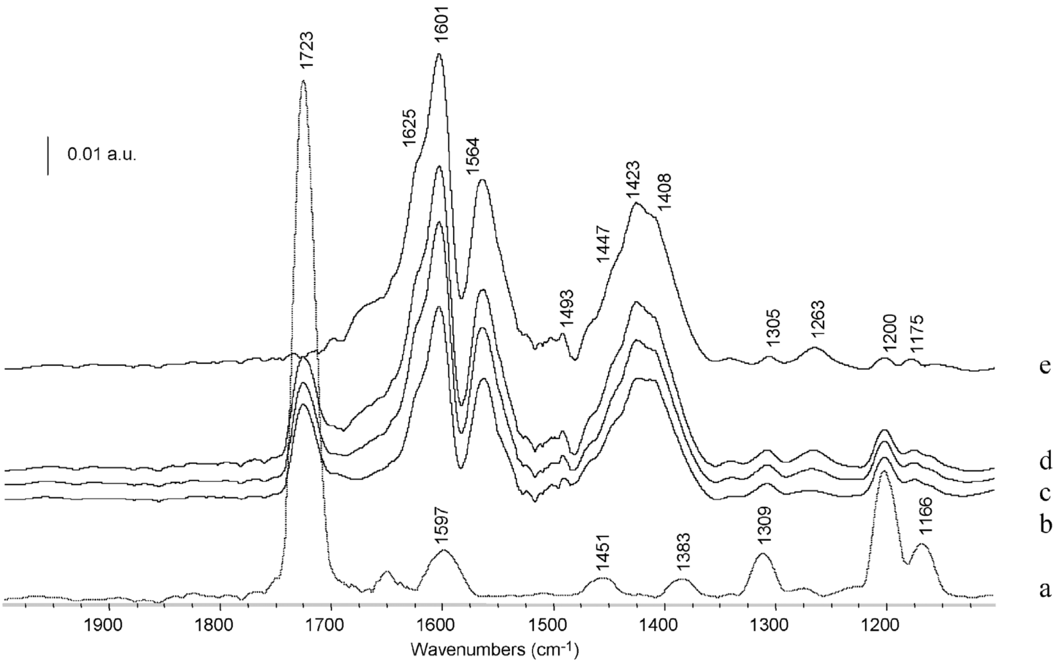
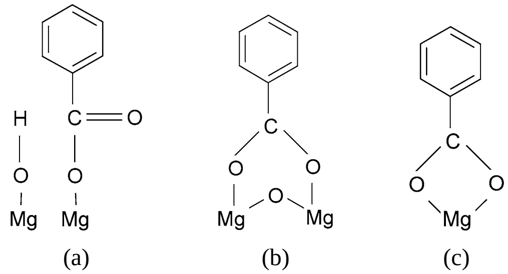


Fig. 5. In situ FTIR spectra of MgO exposed to benzaldehyde at 160 °C for (b) 10 min, (c) 20 min, (d) 30 min and (e) flushing of (d) with N_2 for 30 min. For comparison, the gas phase spectrum of benzaldehyde is shown in (a).



Scheme 6. Proposed structures of surface species formed during the adsorption of benzaldehyde on MgO: (a) carboxylate-like intermediate leading to benzoate formation, (b) bidentate benzoate complex and (c) bridging benzoate complex.

has been assigned to a substituent-sensitive mixed vibrational mode consisting of ring–COH stretching, aldehydic CH bending, CH bending, and C=C stretching [8,9]. Although this band is still visible in the spectra of adsorbed benzaldehyde, its intensity decreased significantly, consistent with a loss of the contribution of the aldehydic group to this mode and the proposed aldehydic hydrogen abstraction during adsorption.

Moreover, a new band grows with time on stream at 1263 cm^{-1}, which is not present in the gas-phase spectrum. Busca [30] reported a shift of the ring–C stretching vibration frequency in toluene from 1210 cm^{-1} in the liquid phase to 1298 cm^{-1} following adsorption on V_2O_5/TiO_2. He attributed this shift to the abstraction of hydrogen from the methyl group during adsorption and concluded that the ring–C bond vibration is very sensitive to its environment. Based on this finding, we can assign the band at 1263 cm^{-1} to the ring–C stretching vibration of the adsorbed benzaldehyde following abstraction of the aldehydic hydrogen.

A strong band at 1564 cm^{-1} and a shoulder at 1408 cm^{-1} in the spectra of adsorbed benzaldehyde are not present in the gas-phase spectrum, indicating the formation of a new surface species. Similar bands have been previously assigned to surface benzoate species formed during the adsorption of benzaldehyde on Al_2O_3 [31,32] and α-Mn_3O_4 [32], or toluene, *o*-xylene, benzaldehyde, and *o*-tolualdehyde on V_2O_5/TiO_2 [19,29]. Differences in the exact frequencies of these vibrations reportedly depend on the nature of the associated surface. More specifically, the two bands at 1562 and 1408 cm^{-1} can be assigned to the symmetric and asymmetric stretching vibrations of a bridging surface benzoate ion coordinated to two surface metal ions, as shown in Scheme 6b [19].

The spectrum of adsorbed benzaldehyde further contains a shoulder at 1423 cm^{-1} that exhibits differences in intensity with time on stream with the other component of this broad band at 1408 cm^{-1}. Furthermore, when the adsorption was carried out at 200 °C, the band at 1423 cm^{-1} grew much more slowly and did not show the same changes in intensity as the 1562 cm^{-1} band, indicating that two different benzoate surface species may be formed. Indeed, Koutstaal et al. [32] assigned a shoulder in this area of the spectrum to the symmetric stretching vibration of a bridging benzoate species formed during the adsorption of benzaldehyde on α-Mn_3O_4 at 300 K. Similar to what we have observed in the current study, this band was found to decrease in intensity with increasing temperature. Kung and McBride [33] reported the presence of two bands in this region during the adsorption of substituted benzaldehydes on iron oxides and assigned them to the symmetric stretching vibration of different benzoate species. These authors suggested that, depending on the substituent groups present, these bands may or may not be resolved. The corresponding asymmetric stretching vibration of the two benzoate species were observed at 1560 and 1495 cm^{-1}, respectively. Finally, van Hengstum et al. [19] assigned two bands at 1500 and 1410 cm^{-1} to a surface benzoate species coordinated to a single surface metal ion as shown in Scheme 6c, formed during the adsorption of benzaldehyde on V_2O_5/TiO_2. Based on these reports, we can assign the band at 1423 cm^{-1} to the symmetric vibration of a second benzoate species, with a structure similar to the one shown in Scheme 6c. A weak band at 1493 cm^{-1} may be assigned to the asymmetric stretching vibration of the same species, although it should be pointed out that features in this frequency range (ca. 1470–1530 cm^{-1}) are very difficult to distinguish due to the strong absorbance of the IR beam by the MgO sample.

Finally, several bands at 1601, 1447, 1306, 1175, and 1160 cm^{-1} are shifted only slightly following adsorption from their corresponding positions in the spectrum of gas-phase benzaldehyde (i.e., 1597, 1451, 1311, 1167, and 1160 cm^{-1}) and can be assigned to pure aromatic ring vibrations, as well as to mixed modes of CH in plane bending and C=C stretching vibrations [10,19,21]. The presence of these bands indicates that the aromatic ring remains intact during the adsorption of benzaldehyde on MgO.

3.5. *Reaction of 2′-hydroxyacetophenone and benzaldehyde*

Spectra collected during the introduction of benzaldehyde onto an MgO sample saturated with 2′-hydroxyacetophenone, as well as during the introduction of 2′-hydroxyacetophenone onto an MgO sample saturated with benzaldehyde, are shown in Figs. 6 and 7, respectively. Following introduction of benzaldehyde (Fig. 6), the band at 1623 cm^{-1} corresponding to the

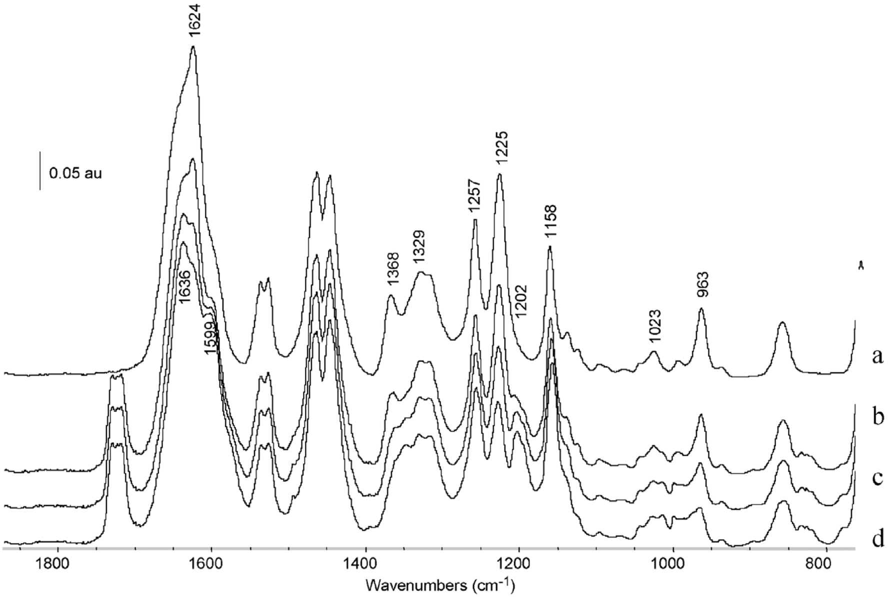


Fig. 6. In situ FTIR spectra of MgO exposed to 2′-hydroxyacetophenone at 160 °C for (a) 30 min followed by subsequent exposure of the adsorbed 2′-hydroxyacetophenone to benzaldehyde for (b) 5, (c) 15, and (d) 30 min.

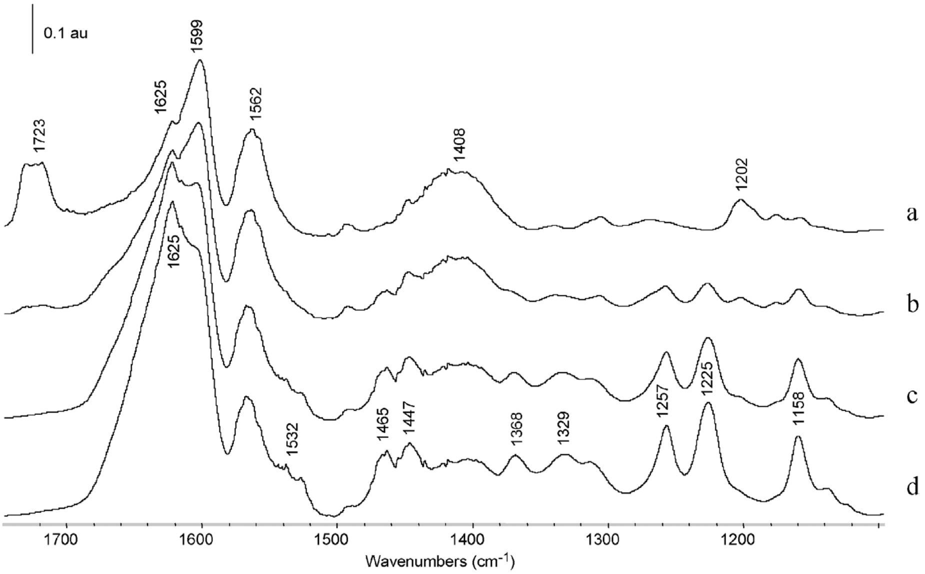


Fig. 7. In situ FTIR spectra of MgO exposed to benzaldehyde at 160 °C for (a) 30 min followed by subsequent exposure of the adsorbed benzaldehyde to 2′-hydroxyacetophenone for (b) 5, (c) 15, and (d) 30 min.

weakened C=O bond of the adsorbed 2′-hydroxyacetophenone and the bands at 1368, 1023, and 963 cm^{-1} characteristic of CH_3 bending and rocking vibrations [8,25] gradually decreased in intensity. Because these bands are stable under desorption conditions (see Fig. 4; spectrum e), this behavior indicates that a reaction occurs between the adsorbed 2′-hydroxyacetophenone-derived phenolate ion and benzaldehyde. In contrast, the intensity of the band at 1329 cm^{-1}, assigned to the C–O bond of the adsorbed phenolate ion, remains unchanged following the introduction of benzaldehyde, since the 2′-hydroxyacetophenone–benzaldehyde reaction to form a chalcone species occurs at the $COCH_3$ group of 2′-hydroxyacetophenone.

A new band at 1635 cm^{-1} is also formed following the introduction of benzaldehyde and grows in intensity with time on stream (Fig. 6). This band is in the typical region of a C=O stretching vibration and can be assigned to the C=O bond present in the 2′-hydroxychalcone product of the 2′-hydroxyacetophenone–benzaldehyde reaction. Two more strong bands at 1723 and 1599 cm^{-1} also grow in intensity following the introduction of benzaldehyde (Fig. 6), but these bands can be assigned to the adsorbed benzaldehyde, as discussed in Section 4. Additional bands assigned to adsorbed benzaldehyde cannot be resolved in the spectra of Fig. 6 due to the strong bands of 2′-hydroxyacetophenone in the same region.

Finally, it should be noted that no benzoate bands are present in the spectra of Fig. 6, suggesting that either the benzoate species or its precursor is active in the reaction with 2′-hydroxyacetophenone. In contrast, upon introduction of 2′-hydroxyacetophenone to a benzaldehyde-saturated MgO sample (Fig. 7), the benzoates bands at 1562 and 1423 cm^{-1} do not decrease in intensity. Furthermore, the chalcone band at 1635 cm^{-1} observed in the spectra of Fig. 6 is not present when 2′-hydroxyacetophenone is introduced to the benzaldehyde-saturated sample, suggesting that a reaction does not occur under these conditions. However, several changes are observed in the spectra of Fig. 7 related to the growth of several bands associated with an adsorbed 2′-hydroxyacetophenone-derived phenolate ion, which quickly (within minutes) replace all of the benzaldehyde-related bands. This behavior is consistent with our earlier observations indicating much stronger adsorption of 2′-hydroxyacetophenone on MgO compared to benzaldehyde. Furthermore, these results suggest that the 2′-hydroxyacetophenone–benzaldehyde Claisen–Schmidt condensation reaction on the MgO surface involves a weakly adsorbed benzaldehyde species and a strongly adsorbed 2′-hydroxyacetophenone-derived phenolate ion.

4. Conclusions

The adsorption of gaseous 2′-hydroxyacetophenone and benzaldehyde on MgO was studied at 160 °C. The results indicate that 2′-hydroxyacetophenone adsorbs on the MgO surface by abstraction of the H atom of the phenolic group, forming a negatively charged phenolate ion. In a subsequent step, a weak bond is formed between the C=O group of the adsorbed phenolate ion and the MgO surface. Benzaldehyde is adsorbed through abstraction of the aldehydic hydrogen. Two different types of benzoate species can also be formed upon destruction of the carbonyl bond. These benzoate species are stable under nitrogen flow and do not react with gaseous 2′-hydroxyacetophenone when the latter is introduced to the IR cell. In contrast, the 2′-hydroxyacetophenone-derived phenolate ion reacts with gaseous benzaldehyde in a reaction resembling the liquid-phase Claisen–Schmidt condensation between these two species.

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