

# A spectroscopic investigation of isopropanol and methylbutynol as infrared reactive probes for base sites on polycrystalline metal oxide surfaces

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## Abstract

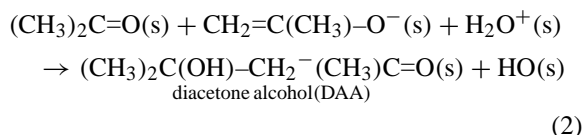
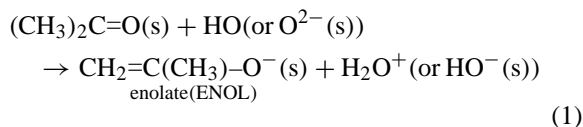
Self-supporting wafers of silica, alumina, titania and zirconia were exposed to gas phase molecules of isopropanol or methylbutynol at different temperatures (up to 400 °C) in situ a specially designed infrared (IR) reactor/cell. Following cooling to room temperature, IR spectra were taken of the gas phase and the wafer, which were subsequently handled automatically to obtain difference spectra of the gas phase and adsorbed products of the alcohol interactions with the oxide surface. The results were discussed for a thorough assessment of the reliability of the application of each of the two alcohols as an IR reactive probe for base sites exposed on the oxide surfaces. The prominent conclusions drawn from the present investigation are the following: (i) adsorptive and catalytic interactions of methylbutynol are more specific to the surface base sites than those of isopropanol, (ii) primary and secondary (further) adsorptive interactions of the alcohol and its decomposition products are more informative than the catalytic interactions, (iii) non-dissociative adsorptive interactions are a better probe of the surface base sites than dissociative ones, and (iv) silica surfaces have no detectable base sites, whereas the other test oxides do have base sites and reveal the following increasing order of basicity: Al < Zr < Ti. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* Metal oxides; Surface basicity; Reactive probes; Isopropanol; Methylbutynol; Infrared spectroscopy

## 1. Introduction

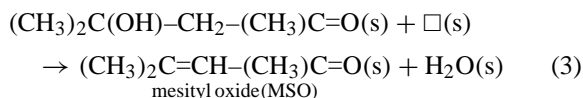
Kinetic catalysis studies [1–3] of hydrogenation of acetone on metal oxide-supported metal particles (Ni, Co and Fe) found the reaction to be a feasible synthetic route to a number of industrially important chemicals, e.g. 4-hydroxy-4-methylpentan-2-one and methyl isobutyl ketone. Recent in situ infrared (IR) studies, performed in this [4,5] and other [6] laboratories, suggested, however, that the availability

of strong Lewis (or Bronsted) basic sites on the oxide support material suppresses the hydrogenation course by indulging the acetone molecules into Aldol-condensation-type side reactions [7]:



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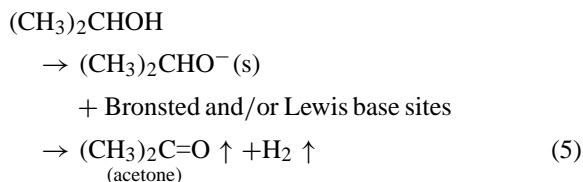
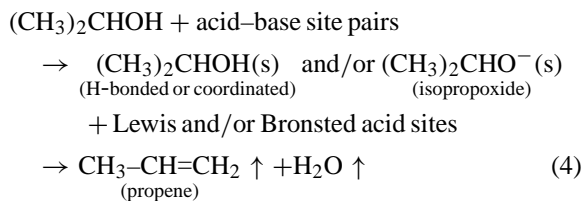


where s is the surface and  $\square$  the vacancy.

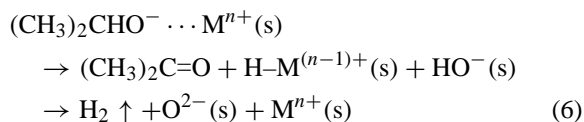
The addition of strong Lewis acid sites to typical basic oxides (e.g.  $\text{Y}^{3+}/\text{MgO}$ ) was found [8] to strengthen the adsorption of acetone condensation products (DAA and MSO), leading eventually to complete blockage of the catalytic centers.

The above account demonstrates the importance of a pre-assessment of the surface basicity of metal oxides to be used as support materials not only for acetone hydrogenation catalysts, but also for catalysts of processes involving condensable (polymerizable) reactants or products [7]. A thorough review of the literature showed that although surface acidity has been studied in much detail [9–11], basicity is more difficult to assess [12,13] and has been less studied [14]. Vibrational spectroscopy of adsorbed probe molecules [9,10,15] and the use of specific test reactions [16] are the techniques frequently applied to examine surface acid–base properties. As stated by Fouad et al. [8], the lack of appropriate acidic probe molecules [15] has limited the applicability of the spectroscopic technique to characterization studies of surface base sites.

The catalytic decomposition of isopropanol (IPrOH) has for long been considered as a test reaction [17,18] in which surface acid sites lead to dehydration (Eq. (4)), while base sites promote dehydrogenation (Eq. (5)):

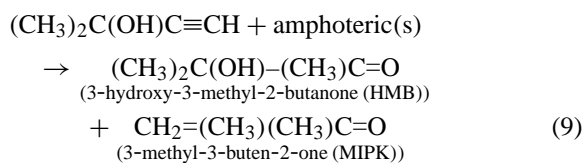
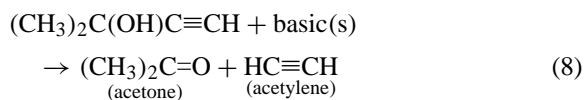
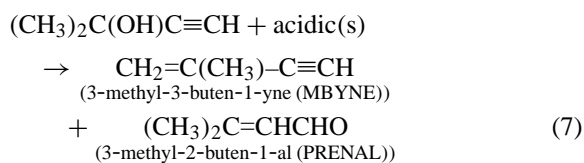


However, availability of surface redox sites ( $\text{M}^{n+}/\text{M}^{(n-1)+}$ ) can also enhance dehydrogenation of the alcohol, as depicted (see Eq. (6)) [18]:



Thus, the dehydrogenation of IPrOH is not solely dependent on the availability of surface base sites. Moreover, the dehydration and dehydrogenation reactions of IPrOH have rather been increasingly utilized to probe the density and chemical properties of acid–base site pairs [7]. The underlying principle is that base site-effected deprotonation of the alcohol is enhanced by acidity of the metal-coordination site of the alcohol molecules [7]. Such cooperative bifunctional interactions may occur in a concerted or sequential mode. Concerted bifunctional pathways require the surface sites involved to coexist within molecular distances, otherwise a rapid transfer of intermediates would lead to kinetic coupling between distant sites and sequential bifunctional pathways [7].

On the other hand, catalytic decomposition of methylbutynol (MBOH) occurs in either of the reaction pathways depicted in Eqs. (7)–(9), depending on the catalyst acid–base properties [16]. It is obvious, that occurrence of the reaction pathway depicted in Eq. (8) would be dependent on the availability of base sites. Despite some successful applications [8,13,16], further reactions of the acetone, thus, produced may render the reaction a less practical probe for base sites.



The present article communicates results of in situ IR spectroscopic studies of interactions of IPrOH and

MBOH gas phase molecules with surfaces of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$  and  $\text{ZrO}_2$ , which have been suggested [4,5] to assume varied surface basicities. Moreover, these test oxides have been widely used [19] in the chemical makeup of potential catalysts for various processes involving organic oxygenates. The present studies were designed to help accomplishing the following objectives: (i) to assess surface basicity of the test oxides, (ii) to characterize high-temperature impacts on the surface reactions, and (iii) to judge the reliability of  $\text{iPrOH}$  and  $\text{MBOH}$  as reactive probes for the surface basicity.

## 2. Experimental

### 2.1. Materials

Test catalysts were ~99% pure Degussa Aerosil-200 (amorphous- $\text{SiO}_2$ ;  $198 \text{ m}^2/\text{g}$ ), Aluminiumoxid C ( $(\gamma + \delta)\text{-Al}_2\text{O}_3$ ;  $107 \text{ m}^2/\text{g}$ ) and P25 titania (anatase- $\text{TiO}_2$ ;  $50 \text{ m}^2/\text{g}$ ), and MEL zirconia ((monoclinic + tetragonal)- $\text{ZrO}_2$ ;  $34 \text{ m}^2/\text{g}$ ). These oxide catalysts, which are respectively denoted below as Si, Al, Ti and Zr for simplicity, were used as supplied.

Reactant molecules were provided by expanded vapors of liquid isopropanol ( $\text{iPrOH}$ ) and methylbutynol ( $\text{MBOH}$ ) at RT; their source liquids were AR-grade products of Baker and Aldrich, respectively. The source liquids were deaerated before application by on-line freeze–pump–thaw cycles performed at liquid nitrogen temperature ( $-195^\circ\text{C}$ ).

$\text{O}_2$  gas, used to burn off surface impurities of the catalysts before exposure to the reactant atmosphere inside the IR-cell (vide infra), was a 99.999% pure product of KOAC (Kuwait) and was used as supplied.  $\text{N}_2$  gas, used to purge the spectrometer (vide infra), was a 99% pure product of KOAC. It was further purified and dried before application, by passing it through appropriate molecular sieve and Oxisorb cartridges.

### 2.2. In situ infrared spectroscopy

An all-Pyrex glass IR-cell equipped with  $\text{BaF}_2$  windows, specially designed for high-temperature measurements [20], was used to facilitate identifying products of the adsorptive and catalytic interactions

of  $\text{iPrOH}$  (or  $\text{MBOH}$ ) gas phase with the test catalysts by in situ Fourier transform infrared (FT-IR) spectroscopy in the transmission mode. A model Spectrum-BX FT-IR Perkin-Elmer spectrometer was used for the measurements (averaged 100 scans at  $4.0 \text{ cm}^{-1}$  resolution), and installed P-E Spectrum v2.0 software was the means whereby spectra acquisition and processing were carried out. The sample compartment was purged with dry  $\text{N}_2$  for 10 min before recording the spectra. Thin ( $20\text{--}30 \text{ mg}/\text{cm}^2$ ), but coherent, self-supporting wafers of the catalyst materials were mounted inside the cell, activated in a stream of  $\text{O}_2$  ( $50 \text{ cm}^3/\text{min}$ ) at  $400^\circ\text{C}$  for 30 min, and, subsequently, outgassed at  $300^\circ\text{C}$ . The temperature was, then, decreased to room temperature (RT) under dynamic vacuum ( $10^{-6}$  Torr), the catalyst and cell background spectra were acquired, and a 10-Torr portion of  $\text{iPrOH}$  (or 2 Torr of  $\text{MBOH}$ ) gas phase was expanded into the cell. The gas/solid interface was maintained at RT for 10 min prior to (i) measuring a spectrum of the gas phase (and cell background), (ii) pumping off the gas phase for 5 min, and (iii) measuring a spectrum of the solid phase (catalyst + adsorbed species). This sequence of measurements was repeated at higher temperatures ( $100\text{--}400^\circ\text{C}$ ), and the spectra were, also, measured after cooling to RT. Difference spectra of gas phase and adsorbed species were obtained by absorption subtraction of the cell and catalyst background spectra, respectively, using the installed software. It is worth noting, however, that the static nature of the measurements is similar to conditions of a slow removal of reaction products (a slow flow-rate) in dynamic systems, in facilitating longer contact times with the catalyst and, hence, further reactions.

## 3. Results and discussion

### 3.1. Background spectra

#### 3.1.1. The reactant molecules

IR spectra taken of gas phase molecules of  $\text{iPrOH}$  and  $\text{MBOH}$  (Fig. 1) display similar absorption bands over frequency ranges of  $\nu\text{O-H}$  ( $3657\text{--}3640 \text{ cm}^{-1}$ ),  $\nu\text{C-H}$  ( $2994\text{--}2885 \text{ cm}^{-1}$ ),  $\delta\text{C-H}$  ( $1462\text{--}1325 \text{ cm}^{-1}$ ),  $\delta\text{O-H}$  ( $\sim 1250 \text{ cm}^{-1}$ ) and  $\nu\text{C-O}/\nu\text{C-C}$  ( $1217\text{--}1072 \text{ cm}^{-1}$ ) bond vibrations [21], as well as distinct

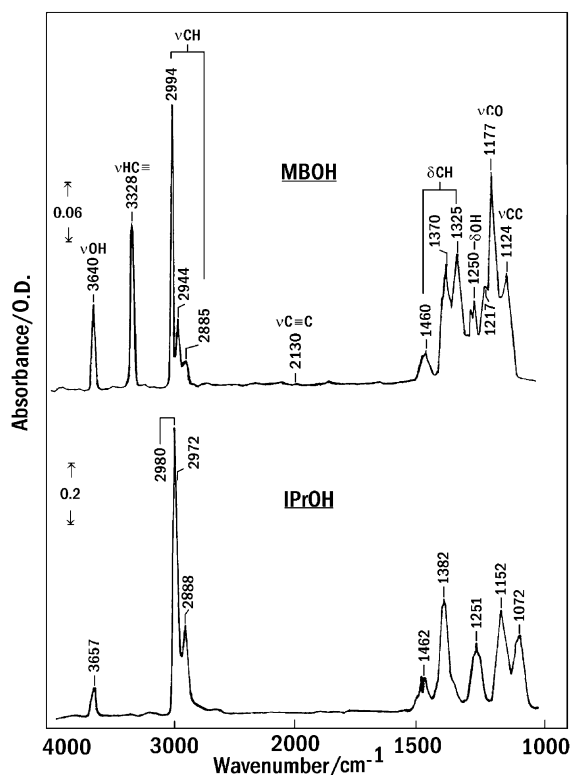


Fig. 1. IR gas phase spectra of a 10-Torr portion of isopropanol (IPrOH) and a 3-Torr portion of methylbutynol (MBOH).

absorptions due to  $\nu\text{H-C}\equiv$  ( $3328\text{ cm}^{-1}$ ) and  $\nu\text{C}\equiv\text{C}$  ( $2130\text{ cm}^{-1}$ ) bond vibrations for MBOH [22].

### 3.1.2. The catalytic surfaces

Background spectra taken of all the catalysts over the full range of frequencies examined ( $4000\text{--}400\text{ cm}^{-1}$ ) were similar in displaying (i)  $\nu\text{O-H}$  absorptions of isolated and associated-OH-groups ( $3800\text{--}3200\text{ cm}^{-1}$ ), (ii) very weak  $\nu\text{CH}$  absorptions (at  $2950\text{--}2850\text{ cm}^{-1}$ ) due to surface species from hydrocarbon impurity, and (iii) very weak absorptions assignable to species ( $\nu\text{CO}_3^{2-}/\text{HCO}_3^-$  at  $1650\text{--}1200\text{ cm}^{-1}$ ) due to carbonate impurity (except for Si). Fig. 2 compares the hydroxyl exhibited by the catalysts at  $4000\text{--}3000\text{ cm}^{-1}$ , and thereby indicates occurrence of various types of isolated OH-groups ( $3800\text{--}3591\text{ cm}^{-1}$ ).

Results reviewed and discussed elsewhere [10,15] may help assigning the absorption maxima resolved

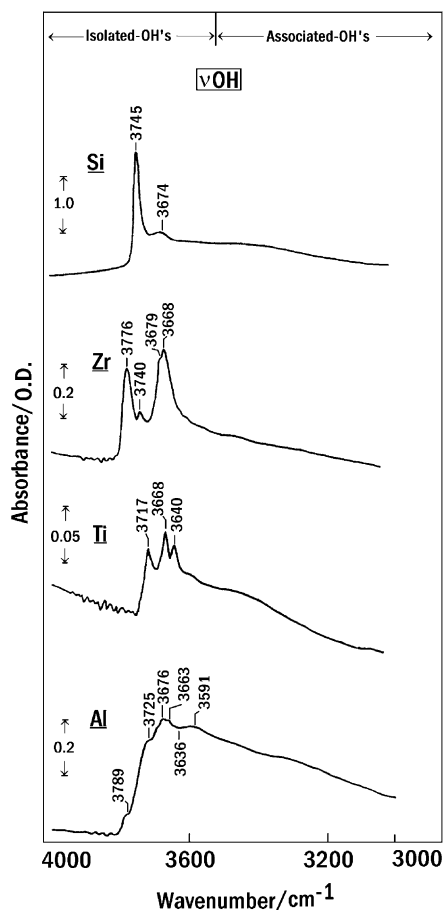


Fig. 2. IR  $\nu\text{OH}$  spectra taken of self-supporting wafers of alumina (Al), titania (Ti), zirconia (Zr) and silica (Si) before exposure to alcohol gas atmosphere.

for Al to terminal ( $3789\text{ cm}^{-1}$ ), bridging ( $3725\text{--}3663\text{ cm}^{-1}$ ) and multi-centered ( $3591\text{ cm}^{-1}$ ) surface Al-OH-groups. The ill-resolved, but strong, absorption at  $3636\text{ cm}^{-1}$  may well be a contribution from  $\nu\text{H-OCO}_2^-$  surface species [23]. It has been concluded [10,15] that the lower the  $\nu\text{OH}$  frequency, the larger the net positive charge (acidity) accumulated on the OH-group. This conclusion was drawn from theoretical structural calculations [24,25] as well as experimental results [9,26]. Consistently, the terminal Al-OH-groups were found incapable of forming H-bonds with CO molecules at liquid nitrogen temperature [26], i.e. having basic character, whereas the bridging and multi-centered Al-OHs were capable of doing so.

On similar grounds, the OH-absorptions observed for Ti (Fig. 2) have been attributed [25–27] to terminal ( $3717\text{ cm}^{-1}$ ) and two different types of bridging ( $3668\text{--}3640\text{ cm}^{-1}$ ) Ti-OHs, with the terminal being less acidic than the bridging-OHs. Two types of isolated OH-groups have also been suggested for Zr [28]: terminal ( $3776\text{ cm}^{-1}$ ) and multi-centered ( $3679\text{--}3668\text{ cm}^{-1}$ ) Zr-OHs. The former has been considered [28] to be basic in nature and the latter acidic, whereas the weak absorption resolved at  $3740\text{ cm}^{-1}$  has been found to relate to impurity of Si-OH-groups. On the other hand, the strong, sharp absorption observed for Si at  $3745\text{ cm}^{-1}$  is due to isolated Si-OH-groups, whereas the broad shoulder centered around  $3674\text{ cm}^{-1}$  is assignable either to bulk-OHs or vicinal surface  $\text{Si}(\text{OH})_2$ -groups [29]. Both types of Si-OHs have been found to assume an obvious acidic character [26].

In earlier IR spectroscopy of adsorbed pyridine and X-ray photoelectron spectroscopy (XPS) studies of the test catalysts [28], the OH coordination sites were identified. Accordingly, trivalent aluminum ions in tetrahedral ( $\text{Al}_t^{3+}$ ) and octahedral ( $\text{Al}_o^{3+}$ ) coordination symmetries were suggested to exist on Al, with the latter being the major site. On the other hand, tetravalent titanium ions belonging to anatase ( $\text{Ti}_a^{4+}$ ) and rutile ( $\text{Ti}_r^{4+}$ ) lattices were implied to occur on Ti, and tetravalent zirconium ions in monoclinic ( $\text{Zr}_m^{4+}$ ) and tetragonal ( $\text{Zr}_g^{4+}$ ) symmetries on Zr, with the former being the major site on the respective oxide. On Si, only tetrahedral ( $\text{Si}_t^{4+}$ ) silicon sites were detectable. These examinations also revealed [28] that basic (terminal) OHs on Al and Zr were activated for a nucleophilic attack on nearby metal-coordinated pyridine molecules at  $\geq 300^\circ\text{C}$ . The resulting species were of  $\alpha$ -pyridine [28]. The occurrence of this chemical transformation has been considered [28] indicative of the presence of acid–base pair sites on surfaces of Al and Zr.

### 3.1.3. Spectra of the gas phase

**3.1.3.1. IPrOH.** Fig. 3 shows IR spectra demonstrating the influence of temperature on the chemical composition of the gas phase at the IPrOH/oxide interface. On Si, the spectra obtained at RT to  $300^\circ\text{C}$  were similar in showing only the bands of IPrOH molecules. At  $400^\circ\text{C}$ , a very weak, but distinct,

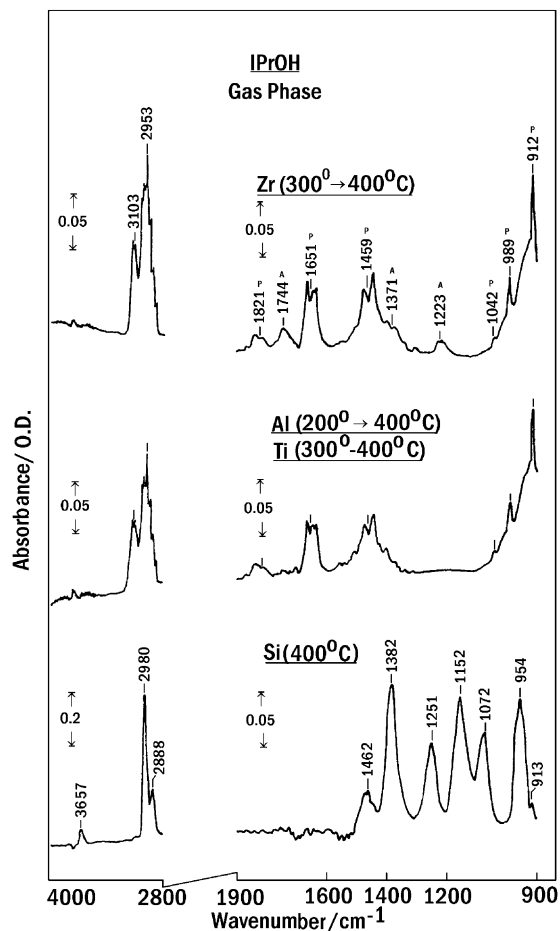


Fig. 3. IR gas phase spectra taken of IPrOH/oxide interfaces at the temperatures indicated. The arrow ( $\rightarrow$ ) means a gradual development with temperature, the hyphen (-) indicates an ultimate change at either temperatures, whereas "A" stands for acetone and "P" for propene.

shoulder was resolved at  $913\text{ cm}^{-1}$ . Thus, IPrOH is largely stable on Si up to  $400^\circ\text{C}$ . On Al and Ti, IPrOH exhibited an identical sequence of conversion at  $200\text{--}400^\circ\text{C}$ , which is expressed in complete dehydration of the alcohol into propene ( $\text{C}_3\text{H}_6$ ) with no sign of formation of acetone molecules (Fig. 3). The sole difference lies in an earlier commencement on Al (at  $\geq 200^\circ\text{C}$ ) than Ti ( $\geq 300^\circ\text{C}$ ). It is to be noted, that the strongest absorption exhibited by propene occurs at a frequency ( $912\text{ cm}^{-1}$ ) very close to that ( $913\text{ cm}^{-1}$ ) at which the sharp shoulder is observed for IPrOH/Si at  $400^\circ\text{C}$ . On Zr, IPrOH remained stable to heating up

to 200 °C. Upon further heating, a considerable proportion of the alcohol was dehydrated into propene at 300 °C, while a minor proportion was dehydrogenated into acetone. The spectrum obtained at 400 °C (Fig. 3) declared a complete conversion of the alcohol into propene (major product) and acetone (minor product).

The above gas phase analysis results indicate that the four test oxides are essentially dehydration catalysts of *i*PrOH, with Si being a much weaker catalyst than the other three. Zr is uniquely shown to dehydrogenate the alcohol to acetone. The dehydration pathway may be represented by Eq. (4), whereas the dehydrogenation activity by Eq. (5) and/or Eq. (6), with the former pathway (Eq. (6)) being less likely on Zr.

In principle, however, surfaces capable of dehydrating and polymerizing alcohols should be equally capable of dehydrogenating alcohols. The common ground is the necessity of base sites for both the dehydration and dehydrogenation activities, as well as nearby cooperative acid site. According to the Eqs. (5) and (6), the dehydrogenation pathway is triggered by a hydrogen abstraction from  $\alpha$ -position in *i*PrOH, either in the form of proton by a Lewis ( $O^{2-}$ ) or Bronsted ( $OH^-$ ) base site, or in the form of a hydride ion ( $H^-$ ) by a reducible Lewis acid site ( $M^{n+}$ ). Even in the former course, a Lewis acid site is necessary to stabilize the carbanion to be formed [18]. Thus, the absence of acetone in the gas phase of *i*PrOH/Al and *i*PrOH/Ti at RT to 400 °C (Fig. 3) may be due, alternatively, to a kinetically frozen desorption of the ketone molecules.

**3.1.3.2. MBOH.** IR spectra were taken of the gas phase of MBOH/oxide at RT to 200 °C (Fig. 4). At 100 °C, weak absorptions emerged at 3452 and 1726  $cm^{-1}$  on Al, Ti and Zr. They grew slightly stronger at 200 °C, while the characteristic bands of MBOH molecules remained the dominant feature in the spectra. On Si, the spectrum obtained at 200 °C remained showing only the characteristic bands of MBOH (Fig. 4). The 1726  $cm^{-1}$  band is assignable to  $\nu C=O$  of carbonyl species, and the 3452  $cm^{-1}$  band is its overtone [21]. The fact that the observed  $\nu C=O$  frequency is ca. 18  $cm^{-1}$  less than that of free acetone molecules (Fig. 3), may suggest a conjugated carbonyl-group (i.e.  $-CO-C=C-$  species) rather than a non-conjugated one. Looking into the

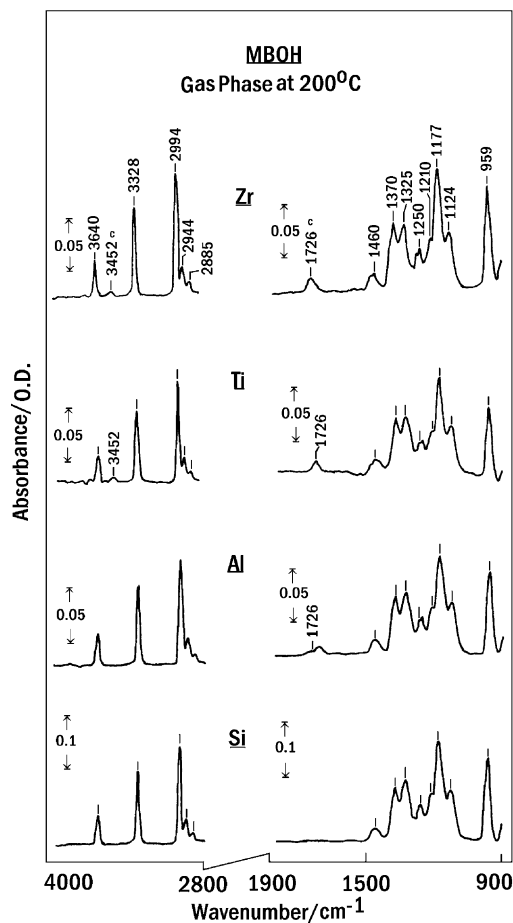
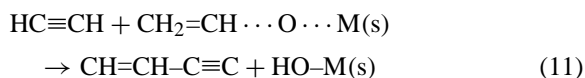
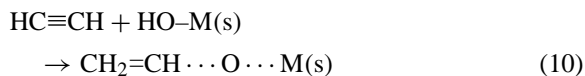
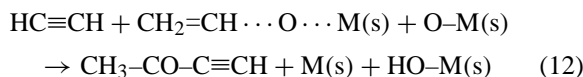


Fig. 4. IR gas phase spectra taken of MBOH/oxide interfaces at the temperature indicated. Letter "C" stands for carbonyl compound.

gas phase of acetylene/MgO at 200 °C, Fouad et al. [13] have acquired IR spectra displaying bands for acetylene plus a strong band at 1740 with a shoulder at 1725  $cm^{-1}$ . They also have provided an experimental evidence to help assigning the shoulder to  $\nu C=O$  of  $CH_3-CO-C\equiv CH$  (acetylacetylene), for which they have suggested the following synthetic route:

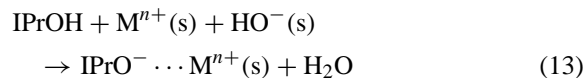




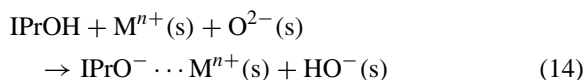
The above results suggest that the decomposition of MBOH on Al, Ti and Zr may occur according to Eq. (8), thus, implying the availability of base sites on these catalysts. The absence of free acetone molecules in the gas phase should not necessarily mean that it was not formed, but possibly that it was not rapidly desorbed into the gas phase. The observed stability of MBOH on Si is rather supportive, since silica does not expose surface base sites [10,29]. A quantitative estimation of the carbonyl compound(s) produced, using the installed software to determine the peak area at  $1726\text{ cm}^{-1}$ , could help ranking the catalysts in the following increasing order of basicity:  $\text{Al} < \text{Ti} \leq \text{Zr}$ . In the following section, only the spectra obtained for the adsorbed species of IPrOH and MBOH on Al, Ti and Zr will be presented and discussed, in the hope of characterizing the surface attributes of the gas phase spectroscopic results.

### 3.1.4. Spectra of the adsorbed species

**3.1.4.1. IPrOH.** IR spectra of the adsorbed species established at IPrOH/oxide interface at RT to  $400^\circ\text{C}$  are partly exhibited in Fig. 5. On Al, the spectra reveal irreversible adsorption of the alcohol at RT to  $200^\circ\text{C}$  in the form of major species giving rise to a number of moderate-to-strong bands at the  $\delta\text{C}-\text{H}/\nu\text{C}-\text{O}/\nu\text{C}-\text{C}$  frequency regions ( $1470\text{--}1100\text{ cm}^{-1}$ ) (see also Fig. 1). These bands are quite similar to those previously observed for IPrOH adsorption on group IVB metal oxides, and assigned to formation of isopropoxide surface species [18]. These species were suggested to form on similarly OH-rich surfaces as depicted by the following equation:



On OH-poor surfaces, the following alternative synthetic course was suggested [18]:



The spectra obtained at RT to  $200^\circ\text{C}$  over the  $\nu\text{OH}/\nu\text{CH}$  frequency regions ( $4000\text{--}2700\text{ cm}^{-1}$ ) ex-

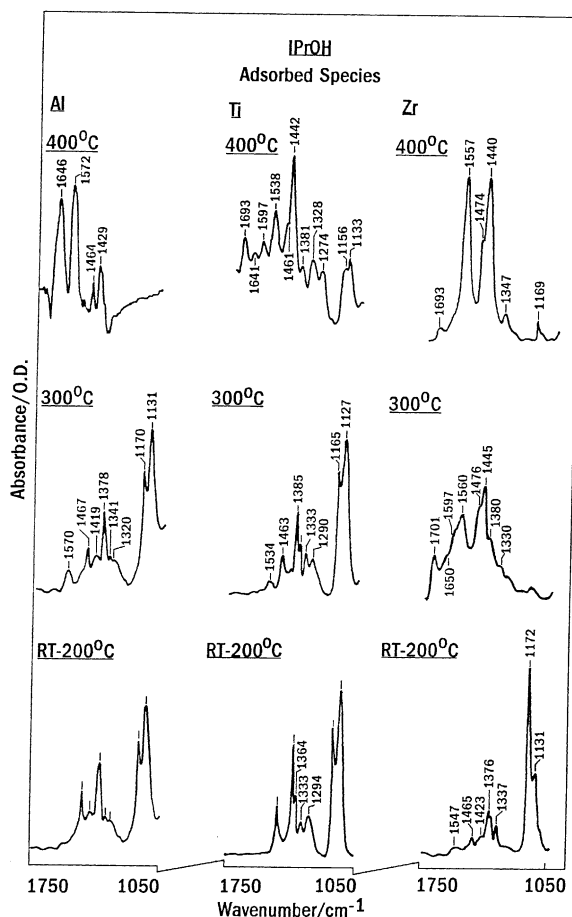


Fig. 5. IR spectra taken of the adsorbed species established at IPrOH/oxide interfaces at the temperatures indicated.

hibited three  $\nu\text{CH}$  absorptions (at  $2990\text{--}2870\text{ cm}^{-1}$ ), a broad band due to associated-OHs (at  $3400\text{--}3200\text{ cm}^{-1}$ ) and the elimination of absorptions due to isolated surface-OHs. The  $\nu\text{OH}/\nu\text{CH}$  spectra obtained for IPrOH/Al are displayed in Fig. 6. The  $\nu\text{CH}$  absorptions are related dominantly to the isopropoxide species [18]. The elimination of absorptions due to isolated Al-OHs is due largely to their H-bonding to IPrOH (and possibly  $\text{H}_2\text{O}$ ) molecules [18], and, to a lesser extent, the consumption of OH-groups in the reaction course (Eq. (13)).

The characteristic absorptions of the isopropoxide species were maintained in the spectrum obtained at the higher temperature of  $300^\circ\text{C}$ , with the emergence of a weak band at  $1570\text{ cm}^{-1}$  (Fig. 5). Similar bands

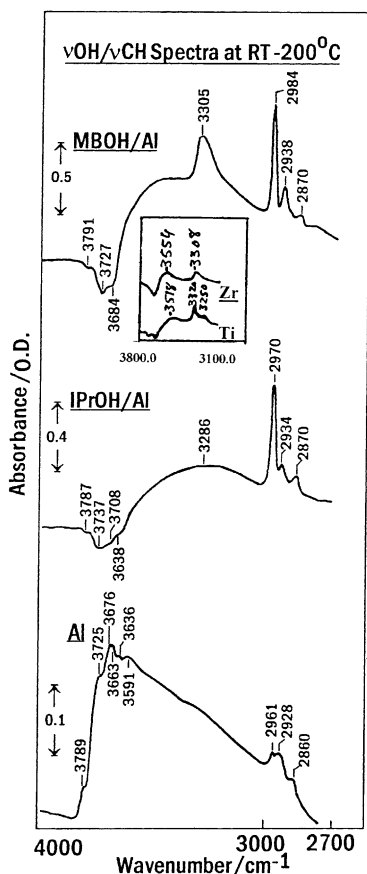


Fig. 6. IR  $\nu\text{OH}/\nu\text{CH}$  spectra taken of Al, and adsorbed species established at its interfaces with IPrOH and MBOH at the temperature range indicated. The inset displays the spectra taken from adsorbed species of MBOH on Zr and Ti.

occurring at  $1600\text{--}1500\text{ cm}^{-1}$  have been assigned to  $\nu\text{C}=\text{O}$  vibrations of conjugated carbonyl-groups, or  $\nu_{\text{as}}\text{COO}^-$  vibrations of carboxylic-groups [30]. Upon increasing the temperature to  $400\text{ }^\circ\text{C}$ , the bands of the isopropoxide species almost completely disappeared, the weak band at  $1570\text{ cm}^{-1}$  grew stronger, and three, presumably relevant, bands emerged at  $1646$ ,  $1464$  and  $1429\text{ cm}^{-1}$  (Fig. 5). The  $1646\text{ cm}^{-1}$  band cannot be assigned to  $\nu_{\text{s}}\text{COO}^-$  vibrations, for it should occur below  $1570\text{ cm}^{-1}$  [30]. Thus, the new  $1646\text{ cm}^{-1}$  band is due also to  $\nu\text{C}=\text{O}$  vibrations, but most likely for non-conjugated carbonyl-groups. On the other hand, bands similar to those occurring at  $1646$  and  $1572\text{ cm}^{-1}$  were observed upon Aldol-condensation

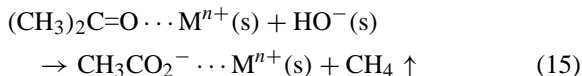
of acetone on basic oxide surfaces, leading to formation of DAA (Eq. (2)) and MSO (Eq. (3)) species [4–6], respectively. Bands similar to those observed at  $1464$  and  $1429\text{ cm}^{-1}$  were attributed to  $\delta\text{CH}_2\text{CO}$  and  $\delta\text{CH}$  vibrations of DAA and MSO species, respectively [4–6]. It is worth mentioning, that in the absence of acetone in the gas phase, the alcohol molecules themselves may get involved in a similar condensation course of reactions on basic sites [7], either through formation of acetone surface species or isopropoxide species.

A behavior quite similar to that of IPrOH/Al was demonstrated by the spectra taken for IPrOH/Ti at RT to  $400\text{ }^\circ\text{C}$  (Fig. 5). At RT to  $200\text{ }^\circ\text{C}$ , the alcohol was shown to adsorb irreversibly as isopropoxide species. The absorptions displayed in the corresponding spectra (Fig. 5) are due solely to these species. They were shown to persist against heating up to  $300\text{ }^\circ\text{C}$  and, partially, at  $400\text{ }^\circ\text{C}$  (Fig. 5). Similar to the case on Al, the spectrum obtained at  $300\text{ }^\circ\text{C}$  resolves a small band at  $1534\text{ cm}^{-1}$  attributable to  $\nu\text{C}=\text{O}$  vibrations of conjugated carbonyl-groups [4–6], or to  $\nu\text{C}-\text{C}-\text{O}^-$  vibrations of enolate species [6]. At  $400\text{ }^\circ\text{C}$ , this band was rendered stronger and slightly shifted to occur at  $1538\text{ cm}^{-1}$ . Moreover, two bands emerged at  $1693$  and  $1597\text{ cm}^{-1}$  due to  $\nu\text{C}=\text{O}$  vibrations of conjugated and non-conjugated carbonyl-groups, and a strong band at  $1442\text{ cm}^{-1}$  and a shoulder at  $1461\text{ cm}^{-1}$  assignable to associated  $\delta\text{CH}_2\text{CO}$  and  $\delta\text{CH}$  vibrations, respectively. The notable strength of the  $1442\text{ cm}^{-1}$  band may be accounted for by a contribution from  $\nu_{\text{s}}\text{COO}^-$  vibrations of carboxylic-groups, while its  $\nu_{\text{as}}\text{COO}^-$  vibration could be behind the enforcement of the absorption at  $1538\text{ cm}^{-1}$ . These results may be attributed to Aldol-condensation products of acetone or the alcohol molecules. It is worth noting, however, that high-frequency  $\nu\text{C}=\text{O}$  vibrations at  $1710\text{--}1690\text{ cm}^{-1}$ , i.e. similar to those responsible for the absorption emerged at  $1693\text{ cm}^{-1}$  at  $400\text{ }^\circ\text{C}$  (Fig. 5), were previously observed for acetone molecules coordinated to surface Lewis sites ( $(\text{CH}_3)_2\text{CO} \cdots \text{M}^{n+}$ ) [4,6]. Unlike the case on Al, however, a partial oxidation to surface carboxylate species appears to occur on Ti.

On similar grounds, the spectra taken of IPrOH/Zr (Fig. 5) also indicate the formation of surface isopropoxide species at RT to  $200\text{ }^\circ\text{C}$ . In contrast, they disclose that Zr surfaces enhance complete conversion of the alkoxide species into condensation carbonyl



products (bands at 1701, 1650, 1597, 1560, 1476, 1445 and 1380  $\text{cm}^{-1}$  [4–6]) and oxidation carboxylate products (bands at 1560, 1445 and 1330  $\text{cm}^{-1}$  [18]). The Zr surfaces are also indicated to be distinct in oxidizing, almost completely, the various surface species into carboxylate species at 400 °C. The dominant band structure monitored in the 400 °C spectrum consists of absorptions (1557, 1474, 1440, 1347 and 1169  $\text{cm}^{-1}$ ) assignable to acetate-groups [18]. A very weak absorption assignable to  $\nu\text{C}=\text{O}$  vibrations of coordinated acetone molecules is also observed at 1693  $\text{cm}^{-1}$ . A facile pathway to the formation of surface acetates would, according to Hussein et al. [18], be via a nucleophilic attack of a surface-OH-group on a nearby metal-coordinated acetone molecule, as depicted by the following equation:



Accordingly, the IPrOH dehydration active sites (Lewis and Bronsted acid sites) are, indeed, capable of catalyzing the alcohol condensation into surface carbonyl compounds (DAA and MSO) as reviewed by Iglesia et al. [7]. Surface acid sites can also initiate Aldol-condensation of ketones and aldehydes [29]. Relatively stronger base sites available on Ti and Zr are capable of initiating IPrOH dehydrogenation into acetone surface species, which are desorbed into the gas phase (on Zr) and/or suffered a surface condensation into carbonyl-containing species (on Zr and Ti). According to Fouad et al. [8], the inability of Ti to release acetone into the gas phase may be attributed to its stronger Lewis acid sites than Zr. As a result, the carbonyl condensation products are strongly adsorbed on Ti, thus, blocking the surface dehydrogenation sites.

**3.1.4.2. MBOH.** IR spectra of adsorbed species of MBOH at RT to 200 °C are partly shown (at 1750–1100  $\text{cm}^{-1}$ ) in Fig. 7. Corresponding spectra obtained over the  $\nu\text{OH}/\nu\text{CH}$  frequency regions (4000–2700  $\text{cm}^{-1}$ ) are exhibited in Fig. 6. The spectra recorded at RT (Figs. 6 and 7) clearly show absorption bands of the various vibrational modes of adsorbed MBOH to be shifted relative to those of the free molecule (Fig. 1). Thus, the  $\nu\text{HC}\equiv$  vibrations appear at 3320–3250  $\text{cm}^{-1}$ , and the  $\nu\text{CH}$  vibrations of the methyl-groups at 2987–2865  $\text{cm}^{-1}$

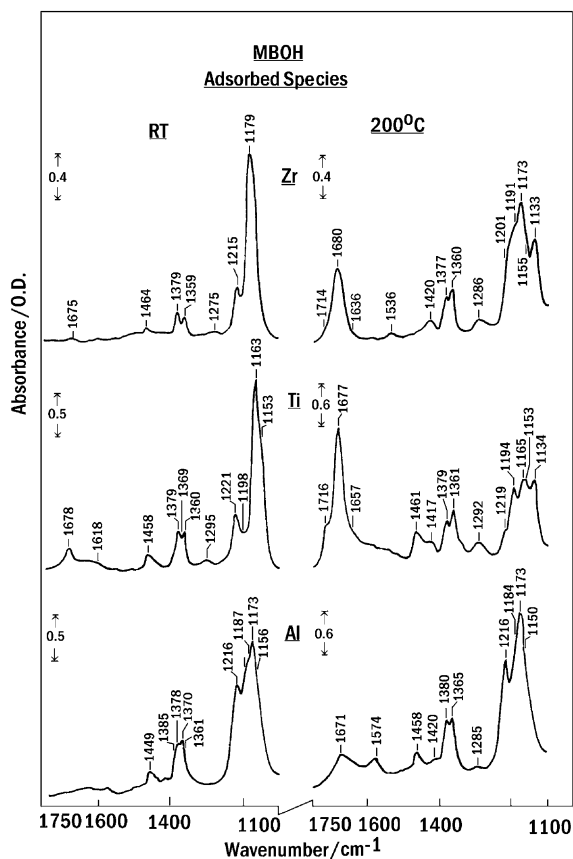
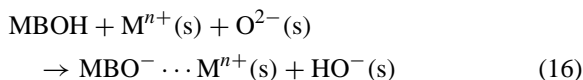


Fig. 7. IR spectra taken of adsorbed species established at MBOH/oxide interfaces at the temperatures indicated.

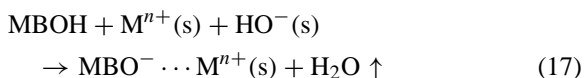
(see Fig. 6 for MBOH/Al). On the other hand, absorption bands due to  $\delta\text{CH}/\nu\text{C}-\text{O}/\nu\text{C}-\text{C}$  are displayed at 1464–1153  $\text{cm}^{-1}$ . Unlike IPrOH, the adsorption of MBOH on Ti and Zr leads to the emergence of a new strong  $\nu\text{OH}$ -absorption at 3554–3518  $\text{cm}^{-1}$  (Fig. 6, inset), which can be attributed to H-bonded OH-groups resulting from the interaction of the alcohol with the surface [8]. It has been reported previously [8,31] that MBOH molecules may be anchored via dissociative adsorption on acid–base ( $\text{M}^{n+}-\text{O}^{2-}$ ) pair sites to form an alkoxide species (methylbutynoxide,  $\text{MBO}^-$ ) and H-bonded OH-groups:



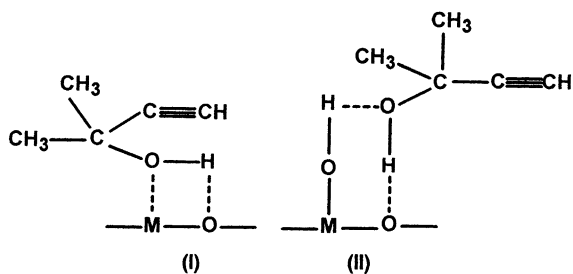
where  $\text{MBO}^-$  is the  $(\text{CH}_3)_2\text{C}(\text{O}^-)\text{C}\equiv\text{CH}$ .

In this process, a strongly basic ( $O^{2-}$ ) site is required to abstract the hydrogen atom from the alcoholic OH, and, simultaneously, the resulting alkoxide-group is anchored to the Lewis acid ( $M^{n+}$ ) site to form the alcoholate species. Consistently, the  $\nu C-O$  vibrations of the adsorbed alcohol species are shown (Fig. 7) to occur at different, but close, frequencies ( $1216-1156\text{ cm}^{-1}$ , Fig. 7) to those of the free alcohol (Fig. 1).

Similarly to *i*PrOH, the elimination of absorptions of isolated surface-OHs (Fig. 6) is indicative of their engagement in H-bonding with MBOH molecules. This may contribute to the broad, extended absorption occurring at  $\leq 3400\text{ cm}^{-1}$ . This behavior is in fact more obvious on Al than on both Ti and Zr (Fig. 6). MBOH molecules have two H-bonding centers, namely the alcoholic OH and the acetylenic-group of free and/or H-bonded molecules. This sort of weak interaction may also lead to the formation of alkoxide species, as depicted by the following reaction equation:



The occurrence of this reaction does not require the strong basicity demanded by the preceding reaction (Eq. (16)). Thus, MBOH molecules may form two different types of H-bonded species (I and II below), in support of a suggestion put forward by Fouad et al. [8]:



The type-I species would dominate on Zr and/or Ti, whereas the type-II species would dominate on Al.

Fouad et al. [8] have also suggested two modes for the adsorptive interactions of MBOH molecules via the acetylenic-group: (i) an interaction with strong Lewis base sites involving the acetylenic hydrogen ( $\equiv C-H \cdots O^{2-}(\text{s})$ ), and (ii) an interaction with Lewis

acid sites involving the  $\pi$ -electrons. These authors have found the former mode of interaction to cause a greater red shift of the  $\nu HC\equiv$  frequency than the latter mode. The present spectra (Fig. 6) display single  $\nu HC\equiv$  absorption on Al (at  $3305\text{ cm}^{-1}$ ) and Zr (at  $3308\text{ cm}^{-1}$ ), but two absorptions on Ti (at  $3320$  and  $3250\text{ cm}^{-1}$ ). It is obvious that the low-frequency absorption observed on Ti (at  $3250\text{ cm}^{-1}$ ) makes a much larger red shift ( $78\text{ cm}^{-1}$ ) than the high-frequency absorptions (at  $3320-3305\text{ cm}^{-1}$ ) do ( $\leq 23\text{ cm}^{-1}$ ). This may indicate that Ti exposes uniquely strong Lewis base sites ( $O^{2-}$ ) capable of bonding the acetylenic hydrogen, and still exposes, similarly to the other oxides, coordinatively unsaturated metal (Lewis acid) sites capable of interacting with the acetylenic  $\pi$ -electrons. This indication is consistent with the dominance on Ti of type-I H-bonded species of MBOH molecules, which has been suggested [8] to involve bonding to base ( $O^{2-}$ ) sites.

Increasing the temperature to  $100^\circ\text{C}$ , and further to  $200^\circ\text{C}$ , caused minor-to-major changes to the RT-spectra of adsorbed MBOH (Fig. 7). The minor changes, which were only observed on Al, were the emergence of two weak bands at  $1671$  and  $1574\text{ cm}^{-1}$ . When correlated with the appearance of a trace amount of acetyl acetylene in the gas phase, these two bands may resemble those observed for *i*PrOH/Al at  $400^\circ\text{C}$  (at  $1646$  and  $1572\text{ cm}^{-1}$ ) in suggesting the formation of a minor proportion of carbonyl condensation products. Fig. 7 also indicates that the major high-temperature-effected changes, which were observed on both Ti and Zr, are reflected essentially in the development of a strong, composite absorption centered around  $1680-1677\text{ cm}^{-1}$ . The origin of this absorption can be traced back to the corresponding RT-spectra, particularly the spectrum obtained for MBOH/Ti (Fig. 7). Moreover, a  $\nu OH$  band was developed near  $3518\text{ cm}^{-1}$ , the  $\nu CH\equiv$  bands were strongly eroded, and a marked complexity was developed in the  $\nu C-O$  absorption which assumed a simpler band structure at RT.

The emerging composite absorption (maximized at  $1680-1677\text{ cm}^{-1}$ ) occurs in the  $\nu C=O$  frequency region, and consists at least of three maxima at  $1716-1714$ ,  $1680-1677$  and  $1657-1636\text{ cm}^{-1}$ . The former two maxima are assignable to adsorbed acetone molecules [4–6], whereas the latter maximum is due to conjugated  $C=O$ -group of acetone condensation

product. The parallel emergence of a weak absorption in the  $\delta\text{CH}_2\text{CO}$  region (at  $1461\text{--}1420\text{ cm}^{-1}$ ) may relate the latter absorption maximum (at  $1657\text{--}1636\text{ cm}^{-1}$ ) to DAA adsorbed species. The reaction Eqs. (1) and (2) may represent the condensation route of acetone into DAA, which requires a base site to abstract hydrogen from  $\alpha$ -position in acetone molecules, and an acid site to stabilize the carbanion thus formed [7]. The complexity developed in the  $\nu\text{C}\text{--}\text{O}$  region ( $1219\text{--}1133\text{ cm}^{-1}$ ) cannot be related to adsorption and condensation of acetone, but rather to an enhancement in the adsorption of MBOH into alkoxide ( $\text{MBO}^-$ ) species.

### 3.1.5. Basicity-dependent alcohol/oxide interactions

The above presented and discussed results reveal that some of the adsorptive and catalytic interactions of IPrOH and MBOH molecules with the metal oxide surfaces demand the availability of base sites, but only a few of them are specific to strong base sites. The following sections characterize and assess basicity-dependent alcohol interactions, in hopes of discerning those specific to strong base sites. It is worth recalling, however, that strong adsorptive interactions are promoting events in catalysis, whereas too strong such interactions could be suppressive [32].

### 3.1.6. Adsorptive interactions

Irreversible adsorptive interactions, whether catalytic or non-catalytic, primary or secondary, are either dissociative or non-dissociative. Dissociative interactions of the present alcohol molecules lead to surface alkoxide species, which are indicative of the availability of acid–base pair sites functioning in a concerted fashion (cf. Eqs. (4), (16) and (17)). Alkoxides are formed on all of the test oxides at RT to  $300^\circ\text{C}$  (except on Si). Accordingly, dissociative adsorptive interactions of the alcohol molecules are not specific to strong base sites.

Non-dissociative adsorptive interactions of alcohol molecules often result in formation of coordinated and H-bonded alcohol molecules [18]. Formation of coordinated molecules depends on the availability of coordinatively unsaturated (CUS) metal sites, and is monitored by the accessibility of  $\delta\text{OH}$  vibrations of  $\text{RO}\text{--}\text{H}$  molecules (at  $1250\text{ cm}^{-1}$ , Fig. 1). Although it could not be unequivocally discerned in the present spectra (Figs. 5

and 7), formation of coordinated alcohol molecules occurs independently of surface base sites. In contrast, H-bonded alcohol molecules are more informative as to the surface basicity, particularly those of MBOH molecules. MBOH molecules have two more centers of weak interactions than those of IPrOH molecules; namely, the acetylenic hydrogen ( $\text{H}\text{--}\text{C}\equiv$ ) and the  $\pi$ -electrons [8]. The former center only binds with strong Lewis base sites ( $\text{O}^{2-}$ ), causing the  $\nu\text{H}\text{--}\text{C}\equiv$  vibration frequency to suffer a larger red shift than that rendered by the  $\pi$ -electrons interaction with Lewis acid sites ( $\text{M}^{n+}$ ). Therefore, the relatively much larger  $\Delta\nu\text{H}\text{--}\text{C}\equiv$  ( $78\text{ cm}^{-1}$ ) observed for MBOH/Ti must probe relatively stronger Lewis base sites on Ti than both Zr and Al ( $\Delta\nu\text{HC} \leq 23\text{ cm}^{-1}$ ). Therefore, adsorptive interaction of MBOH via the acetylenic hydrogen is quite specific to strong base sites. The H-bonding, which is a common mode of adsorptive interactions of IPrOH and MBOH, leads to formation of the type-I (on  $\text{M}\text{--}\text{O}$  pair sites) and type-II (on  $\text{HO}\text{--}\text{O}$  pair sites) species sketched (for MBOH) above. Formation of type-I species demands the availability of Lewis base sites, and is monitored by the emergence of  $\nu\text{OH}$ -absorption of associated hydroxyl-groups similar to that observed at  $3554\text{--}3518\text{ cm}^{-1}$  on Ti and Zr (Fig. 6, the inset). In contrast, formation of type-II species is much less basicity demanding, and gives rise to a less defined absorption at low  $\nu\text{OH}$  frequency ( $\leq 3400\text{ cm}^{-1}$ ) as observed on Al (Fig. 6).

Secondary adsorptive interactions of primary adsorbed species (at  $>\text{RT}$ ), which are mostly Aldol-condensation [7] of the alcohol molecules (essentially, IPrOH) and/or their decomposition products: acetone (Eqs. (5) and (6)) and acetyl acetylene (Eqs. (10) and (12)), require a strong base site to abstract hydrogen from  $\alpha$ -position in the ketone or alcohol molecules, and a Lewis acid site to stabilize the carbanion, thus, formed (cf. Eqs. (1)–(3)). Thus, the availability of strong acid–base pair sites leads to a very strong adsorption of the surface intermediates of Aldol-condensation (enolate, DAA and MSO species) and a consequent suppression of the catalytic activity. IPrOH is shown to be the main precursor of condensation reactions on surfaces of all of the test oxides, with a possible contribution from its dehydrogenation product (acetone) on Ti and Zr. In contrast, decomposition products of MBOH (acetone and acetyl

acetylene) are the main precursors, which polymerize selectively to DAA surface species. Acetone is shown to remain largely on the surface rather than in the gas phase (Fig. 7). Hence, the secondary adsorptive interactions sustain the primary ones in suggesting that Ti does expose not only strong Lewis base sites ( $O^{2-}$ ), but also strong Lewis acid sites (CUS  $Ti^{4+}$ ). They show, moreover, that Zr also exposes strong Lewis base sites, but weaker Lewis acid sites. Zr was the sole test oxide on which the dehydrogenation product of IPrOH (i.e. acetone) was desorbed into the gas phase (Fig. 3). Zr also was the oxide on which the relatively largest amount of carbonyl-containing products of decomposition of MBOH was released into the gas phase (Fig. 4).

### 3.1.7. Catalytic interactions

Catalytic interactions of alcohols on metal oxide surface are essentially dehydrating, and, accordingly, lead to formation of corresponding alkenes [18], as propene is formed from IPrOH on Al, Ti and Zr (Fig. 3), or alcohol condensation products. Iglesia et al. [7] have reported that the alcohol dehydration activity implies that the surface contains acid–base pair sites capable of catalyzing alcohol condensation reactions. If strong base sites, or redox Lewis sites (Eq. (6)), are available on the surface, then alcohol dehydrogenation activity is developed (case of IPrOH/Zr), as well as Aldol-condensation activity towards the dehydrogenation product (case of MBOH on Ti and Zr). The static nature of the present measurements would allow sufficient contact time for the dehydrogenation products to react further with the surface. The observance of dehydrogenation and condensation products on the surface, but not in the gas phase, means that the surface exposes strong acid–base pair sites capable of suppressing their desorption and, hence, the catalytic activity. Thus, unlike earlier reports [17,18], the absence of alcohol dehydrogenation products in the gas phase should not always mean absence of base sites on the surface.

## 4. Conclusions

The following conclusions may be drawn from the above presented and discussed results:

1. Application of IPrOH and MBOH as IR reactive probes of surface base sites could be quite informative, provided that both the gas phase and surface species are examined.
2. Catalytic and adsorptive interactions of MBOH are generally more specific to the surface basicity than those of IPrOH.
3. Adsorptive interactions of the alcohol are more informative and reliable than the catalytic ones alone, with the non-dissociative adsorptive interactions being more basicity specific than the dissociative ones.
4. Non-dissociative, primary adsorptive interactions of MBOH probe the presence of Lewis base sites ( $O^{2-}$ ) when they lead to formation of molecules anchored to the surface via the following two modes of interactions: (i) simultaneous interactions with  $M^{n+}$  and  $O^{2-}$  sites (type-I species), and (ii) interactions between acetylenic hydrogen and  $O^{2-}$  sites, with the latter being rather specific to strong base sites.
5. Surface base sites may develop secondary adsorptive interactions (Aldol-condensation type) involving molecules of alcohol (essentially IPrOH) and alcohol decomposition products (acetone and acetylene). When products (DAA, MSO and/or acetyl acetylene) are not rapidly desorbed (i.e. not observed in the gas phase), the surface is considered to also contain strong Lewis acid sites functioning in a concerted fashion to stabilize the surface intermediates.
6. The absence of acetone and acetylene gas phase products despite the availability of surface base sites is indicative of coupling of the base sites with strong acid sites.
7. Accordingly, Si is found not to expose detectable surface base sites, whereas Al, Ti and Zr do. Lewis base sites exposed on Ti are found to be stronger than those on Zr, which are still stronger than those on Al (if any).

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