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Methylacetylene and *tert*-butylacetylene as IR-probe molecules for the characterisation of basicity

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Dedicated to J.C. Lavalley on the occasion of his 60th birthday

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Abstract

Methylacetylene (MA) and *tert*-butylacetylene (TA) were used as probe molecules in infra-red spectroscopy for characterisation of the basicity of MgO. Reference experiments with SiO_2 showed the formation of a π-complex via the C≡C bond of MA or TA with the weakly acidic silanol groups. The adsorption model proposed for MA and TA on MgO involves a H-bonding adsorption interaction of the probe molecule via the acidic ≡CH end with the basic O^{2-} sites with a possible simultaneous interaction of the C≡C bond with OH groups which are preferentially located at corners on the MgO surface.

Keywords: Basicity; IR-probe molecules; MgO; Acetylenes

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1. Introduction

An increasing interest has developed in the basic properties of oxide catalysts which are used either as solid catalysts or as supports. Adsorption of small and weakly interacting probe molecules in combination with vibrational spectroscopy is a widely used technique to study the acido-basic properties of the surface of a catalyst [1]. In such investigations adsorption-induced alterations of infra-red frequencies and intensities of the probe are related to properties of the exposed sites [1]. Lavalley [2] published a critical review of different probe molecules used to study surface basicity of metal oxides such as CO, CO_2, pyrrole, chloroform, thiols, etc. It was shown that this method has its limitations since none of the mentioned probe molecules can be universally used. However, some studies have been carried out using hydrocarbon molecules as probe [3–5], and a recent study on methane adsorption [4] on MgO combining Fourier transform infra-red (FTIR) spectroscopy and density functional cluster model calculations indicated that the interaction occurs preferentially with Lewis acid sites Mg^{2+} and more weakly with O^{2-} corner sites. The first results published by Uvarova et al. [5] concerning the use of acetylene seemed very promising. In this study, the ν(≡CH) stretching frequency was shown to shift to lower frequencies when acetylene is adsorbed, and the shift appeared to be sensitive to the strength of basic sites of a series of sodium zeolites. A subsequent study by Lavalley et al. [6] using but-1-yne as probe molecule at room temperature on a series of zeolites showed the same trend of the ν(≡CH) shift. In the present work, we

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chose to cope with the problem of the two coupled $\nu(\equiv CH)$ stretching vibrations in acetylene by taking methylacetylene (MA) as probe molecule. Huber [7] and Knözinger and Huber [8] proposed a model of adsorption of MA on MgO; the $\nu(\equiv CH)$ and $\nu(C\equiv C)$ normal modes were found to strongly shift to lower wavenumbers when H-bonded species were formed while only small shifts occurred in the case of the formation of a π-complex. As MA can react with both Lewis acid and basic sites simultaneously (σ- and π-adsorption), we also chose another sterically more hindered molecule, namely *tert*-butylacetylene (TA) in order to avoid π-complexes detecting Lewis sites. The aim of the present paper is to determine to which extent mono-substituted acetylenes such as MA or TA can be used as probe molecule for basicity of oxide catalysts in general and of MgO in particular.

Magnesium oxide has received great attention because of its common use as a catalyst or as catalyst-support for many reactions, including isomerisation, hydrogenation, oxidation and elimination of functional groups [9]. The electropositivity of the magnesium atoms gives MgO basic properties and because of its irregular surface (steps, kinks, edges and other defects) the oxygen anions (basic Lewis centres) have different coordination states (3c, 4c and 5c), where the 3c-coordinated oxygens are considered to be the most basic ones [10,11]. Silica was also studied as a reference so as to analyse the behaviour of MA and TA when interacting with weak Brønsted acid sites (silanol groups).

2. Experimental

2.1. MgO

For the preparation of magnesium oxide, magnesium hydroxide $Mg(OH)_2$ (pure, Merck) was used. The calcination programme of $Mg(OH)_2$ leading to MgO was as follows:

$$\mathrm{RT} \rightarrow 300^\circ\mathrm{C}\ (5^\circ\mathrm{C}\ min^{-1}) \rightarrow 350^\circ\mathrm{C}\ (2^\circ\mathrm{C\,min}^{-1}, 2\,\mathrm{h}) \rightarrow 600^\circ\mathrm{C}\ (2^\circ\mathrm{C\,min}^{-1}, 4\,\mathrm{h}) \rightarrow \mathrm{RT}$$

The resulting MgO has a specific surface area of $151\,m^2\,g^{-1}$ and the size of the crystallites as calculated from XRD data using the Scherrer equation was 10–11 nm.

2.2. SiO_2

A commercial silicon oxide (99.8%) from Ventron was used for this study. It is a very light powder and its specific surface area is $195\,m^2\,g^{-1}$. Silica has weak Brønsted acidic properties due to the silanol groups on the surface.

2.3. Probe molecules for characterisation of basicity: MA and TA

MA (Me–C≡CH, prop-1-yne, 97%, Lancaster) and TA (3,3-dimethyl-1-butyne, 98%, Lancaster) were used as probe molecules for the characterisation of basic sites.

2.4. FTIR spectroscopy

IR studies were carried out with a Bruker IFS 88 spectrometer and spectra manipulations were carried out using the OPUS program (Bruker). Self-supporting wafers ($5–10\,mg\,cm^{-2}$) were prepared by pressing the powder at a pressure of 10^4 kPa. The wafers were then directly placed in the purpose-made transmission cell and heated in situ according to the following pretreatment procedure:

$$\mathrm{RT} \rightarrow 500^\circ\mathrm{C}\ (\mathrm{O_2}, 5^\circ\mathrm{C\,min}^{-1};\ \mathrm{vacuum}, 1.5\,\mathrm{h})$$

We present the spectra as difference spectra by subtracting the spectrum recorded prior to adsorption. The adsorption of MA and TA was carried out at room temperature.

3. Results

The spectrum of species formed upon adsorption of MA and TA mainly presents bands in the region 3800–3350 [$\nu(OH)$], 3330–3300 [$\nu(\equiv CH)$], 3020–2850 [$\nu(CH_3)$, $2\delta(CH_3)$] and 2140–2100 cm^{-1} [$\nu(C\equiv C)$]. The exact values observed for $\nu(\equiv CH)$ and $\nu(C\equiv C)$ of MA and TA in the vapour phase are summarised in Table 1. After adsorption of the probe molecule, shifts of the $\nu(\equiv CH)$ and $\nu(C\equiv C)$

Table 1
Stretching band of MA and TA (gas phase), $\nu(\equiv\text{CH})$ and $\nu(\text{C}\equiv\text{C})$

	$\nu(\equiv\text{CH})$ (cm^{-1})	$\nu(\text{C}\equiv\text{C})$ (cm^{-1})
MA	3334	2138
TA	3334	2128

bands as well as large shifts of the ν(OH) bands were observed. These shifts provide information on the perturbation of the surface OH groups by the adsorption of the probe molecule.

3.1. SiO_2

3.1.1. MA adsorption on SiO_2

Fig. 1 shows the 3900–1900 cm^{-1} range spectrum (difference) of species formed on the adsorption of 5 kPa MA on SiO_2. The intensities of the bands grow with increasing pressure of the adsorbed vapour. The sites are saturated at 15 kPa MA. As the spectrum represents the subtraction of the spectrum obtained after adsorption and the original spectrum of silica, the negative band observed at 3747 cm^{-1} is caused by the perturbation of the ν(OH) stretching band (silanol groups), while a new much broader and intense band grows in at 3575 cm^{-1}. The red-shift of the ν(OH) stretching band is 172 cm^{-1}. The shifted band is broad and symmetric and the integrated intensity is significantly enhanced as compared to the original band at 3747 cm^{-1}, these features being characteristic of H-bonding. The $\nu(\equiv\text{CH})$ stretching band at 3312 cm^{-1} is narrow and is red-shifted relative to the vapour phase frequency by 22 cm^{-1}. The $\nu(CH_3)$ and $2\delta(CH_3)$ bands between 3020 and 2850 cm^{-1} are weak and are not shifted relative to their vapour phase positions, indicating that the methyl group of MA is not perturbed by the adsorption. The $\nu(\text{C}\equiv\text{C})$ stretching band at 2127 cm^{-1} is also weak and is red-shifted by 11 cm^{-1} relative to the vapour phase position.

3.1.2. TA adsorption on SiO_2

When 1.5 kPa TA is adsorbed on SiO_2, the resulting spectrum (Fig. 2) is closely analogous to that observed for adsorption of MA. The ν(OH) stretching band of free hydroxyl groups is observed at 3748 cm^{-1}. Its intensity decreases when the TA pressure increases.

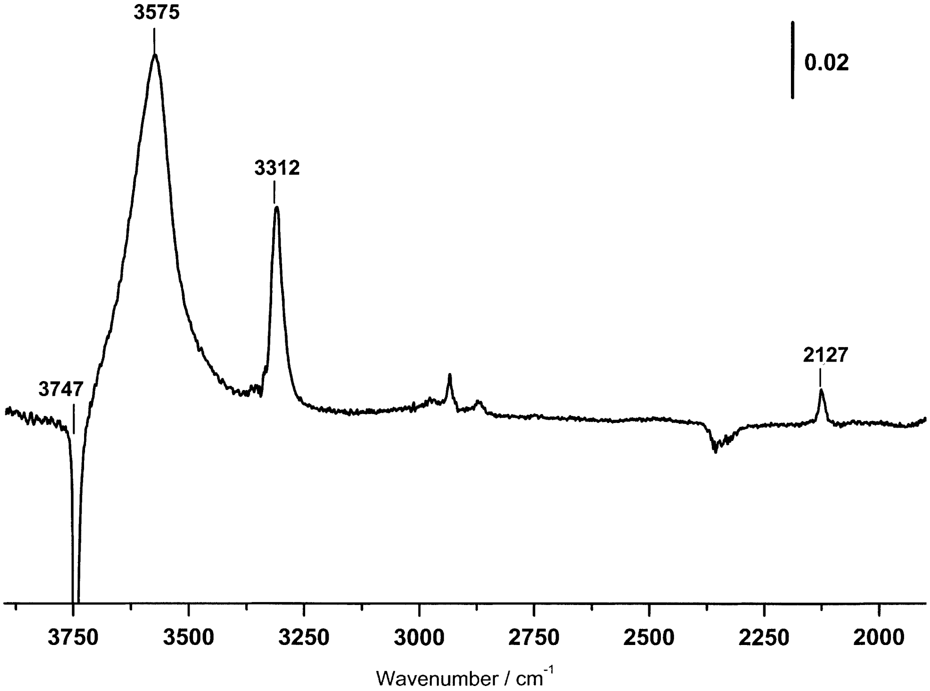


Fig. 1. IR spectrum of species formed by MA adsorption (5 kPa) on SiO_2. (The negative band near 2300 cm^{-1} is an artefact caused by gas phase CO_2.)

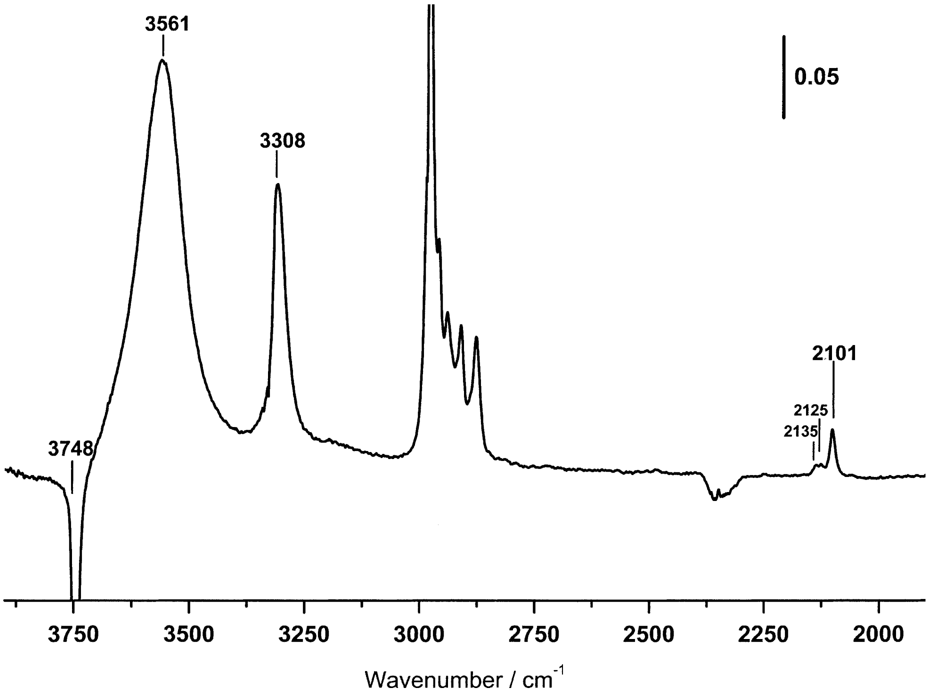


Fig. 2. IR spectrum of species formed by TA adsorption (1.5 kPa) on SiO_2. (The negative band near 2300 cm^{-1} is an artefact caused by gas phase CO_2.)

A broad shifted ν(OH) band appears at 3561 cm^{-1} ($\Delta\nu = -187\,cm^{-1}$) when TA adsorbs. The ν(≡CH) band at 3308 cm^{-1} is red-shifted by 26 cm^{-1} relative to its gas phase position. The band is narrow and intense. The methyl group stretching vibration bands are very intense but are not shifted. The ν(C≡C) stretching bands in the 2140–2100 cm^{-1} region exhibit a difference as compared to the MA spectrum because three bands bands are observed (Figs. 2 and 3). The major band at 2101 cm^{-1} is sharp and red-shifted by 27 cm^{-1} relative to its vapour phase position at 2128 cm^{-1}. Two weak bands located at 2125 and 2135 cm^{-1} are attributed to combination bands, which are also observed in the vapour phase spectrum and not shifted on adsorption of the TA molecule.

3.2. MgO

3.2.1. MA adsorption on MgO

The spectrum of 5 kPa MA adsorbed at room temperature on MgO is shown in Fig. 4. The MA adsorption leads to the appearance of at least two poorly resolved ν(OH) bands at 3693 and 3588 cm^{-1} which are red-shifted by 62 and 167 cm^{-1}, respectively, relative to the unperturbed band at 3755 cm^{-1}, the intensity of which decreases when the MA pressure increases. The ν(≡CH) band is characterised by a large width and intensity and by the fact that two red-shifted bands can be distinguished at 3268 and 3147 cm^{-1} ($\Delta\nu = -66$ and $-187\,cm^{-1}$, respectively) suggesting two different adsorption species of MA on the MgO surface, which induce shifts to lower wavenumbers relative to the vapour phase of the ν(≡CH) band. The stretching vibration bands of the CH_3 group in the 3020–2850 cm^{-1} region do not show any detectable frequency shift. The ν(C≡C) vibration mode appears at 2121 cm^{-1} ($\Delta\nu = -17\,cm^{-1}$) as a sharp and relatively intense band.

3.2.2. TA adsorption on MgO

Fig. 5 shows the spectrum recorded after adsorption of 1.5 kPa of TA on MgO at room temperature. Besides the ν(OH) vibration band at 3758 cm^{-1} decreasing with increasing TA partial pressure, we observe a very broad shifted ν(OH) band containing at least three main bands at 3682, 3621 and 3488 cm^{-1}

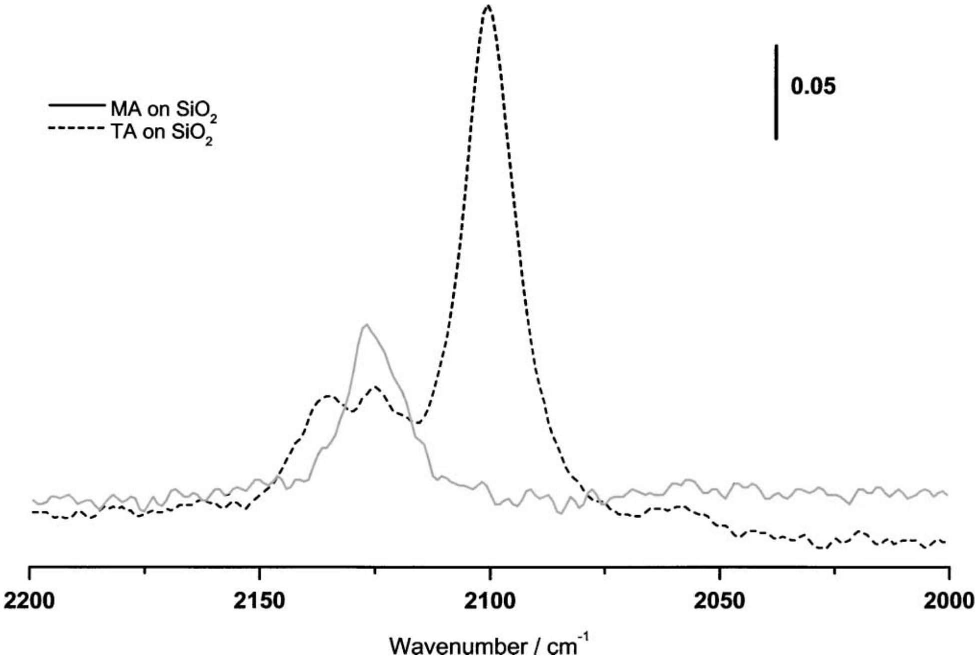


Fig. 3. 2200–2000 cm^{-1} wavenumber region of the spectra of MA and TA adsorbed on SiO_2.

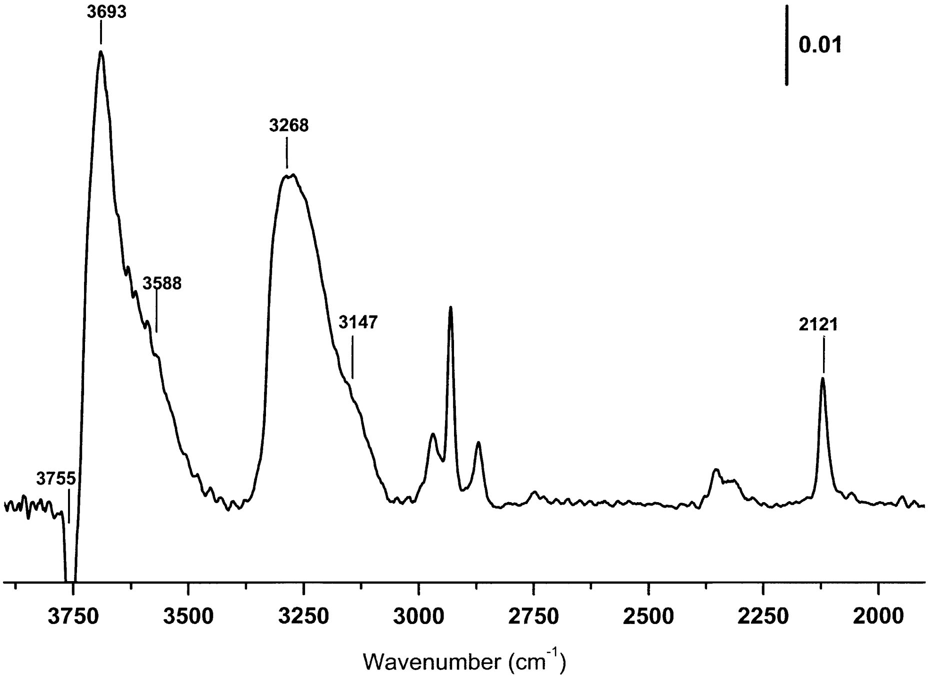


Fig. 4. IR spectrum of species formed by MA adsorption (5 kPa) on MgO.

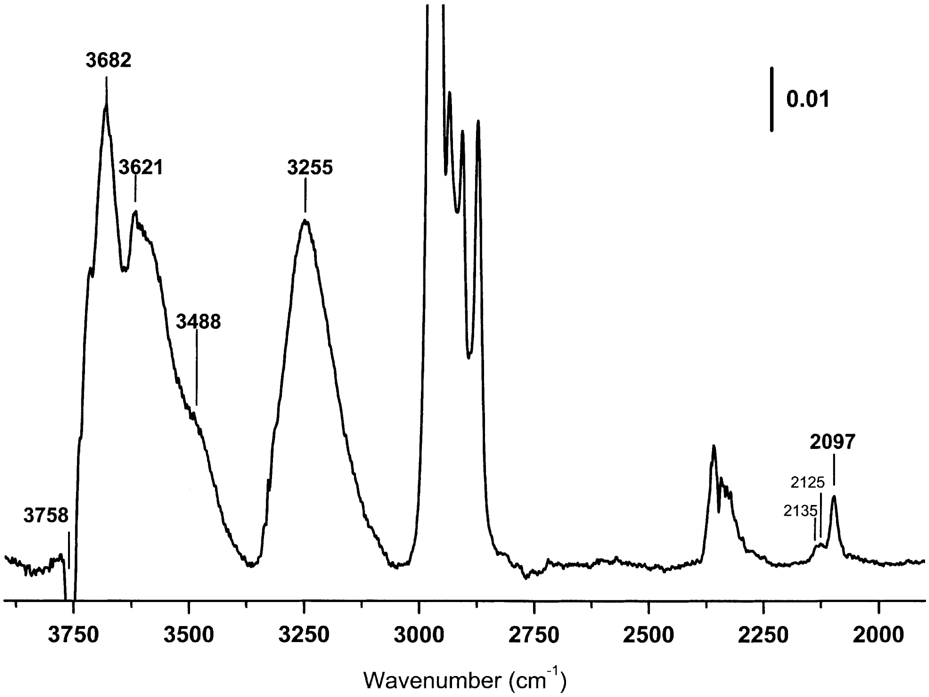


Fig. 5. IR spectrum of species formed by TA adsorption (5 kPa) on MgO.

($\Delta\nu = -76, -137$ and $-270\,cm^{-1}$, respectively). The $\nu(\equiv CH)$ mode at $3255\,cm^{-1}$ seems to be more symmetric than that of MA adsorbed on MgO. The observed red-shift relative to the vapour phase frequency is $-79\,cm^{-1}$. The band is very broad and exhibits a strongly enhanced integrated intensity. The methyl stretching vibration bands in the 3020–2850 cm^{-1} region are very intense and do not show any shift relative to the gas phase. At lower wavenumbers three are detected as in the case of SiO_2. The position of the major band at 2097 cm^{-1} is well defined and undergoes a shift of $-31\,cm^{-1}$. The two weak bands at 2135 and 2125 cm^{-1} are not shifted and are attributed to combination bands as suggested before.

4. Discussion

4.1. SiO_2

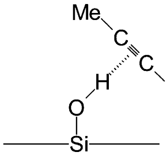
The adsorption of both MA and TA on SiO_2 has a significant effect on the $\nu(OH)$ stretching vibration band, as indicated by the fact that the O–H stretching band at 3747 cm^{-1} decreases in intensity and that the shifted band of surface silanol groups at 3575 cm^{-1} for MA and 3561 cm^{-1} for TA induced by the adsorption of the probe molecule are very broad and intense. This implies that MA and TA adsorb analogously on SiO_2. The data summarised in Table 2 clearly indicate relatively small red-shifts and small full width at half maximum (FWHM) values of the $\nu(\equiv CH)$ band suggesting that the CH-group is not directly involved in the adsorption interaction. Therefore, it is inferred that most likely the adsorption of MA and TA occurs via a H-bonding type interaction between a silanol group and the acetylenic triple bond (π-bonding). Model structures of the adsorption species of MA and TA are shown in Schemes 1 and 2, respectively.

4.2. MgO

Acetylene adsorption on MgO (1 0 0)-single crystal surfaces at temperatures below 100 K has been reported [12,13]. Semiempirical potential calculations

Table 2
FWHM of the stretching bands and shifts of the $\nu(\equiv\text{CH})$ and $\nu(\text{C}\equiv\text{C})$ bands of MA and TA adsorbed on SiO_2 and MgO at room temperature

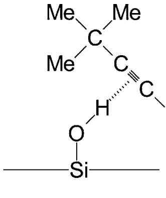
		FWHM (cm^{-1})			Shift (cm^{-1})		
		ν(OH)	$\nu(\equiv\text{CH})$	$\nu(\text{C}\equiv\text{C})$	ν(OH)	$\nu(\equiv\text{CH})$	$\nu(\text{C}\equiv\text{C})$
SiO_2	MA	123	40	47	−172	−22	−11
	TA	124	41	68	−187	−26	−27
MgO	MA	96	140	20	−62/−167	−66/−187	−17
	TA	178	121	19	−76/−270	−79	−31



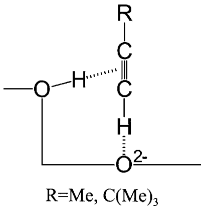
Scheme 1. Model of the adsorption of MA on SiO_2.

combined with dynamical LEED experiments suggested that acetylene was physisorbed under these conditions in an ordered overlayer. The results suggested that the acetylene lies almost parallel to the surface in a herring-bone structure. Barteau and his coworkers [14,15] also demonstrated that acetylene is physisorbed on defect-free Mg (1 0 0) surfaces with dissociative chemisorption not occurring. In contrast, when acetylene was adsorbed on sputtered MgO [16] and on nano-sized MgO [16] exposing edge and corner sites the molecule did dissociate and formed surface acetylide groups at room temperature and below. Acetylene also showed significant reactivity when adsorbed on yttrium-modified MgO [17].

In the present study using MA and TA as probe molecules no indications for reactive chemisorption were found. We therefore infer that molecular adsorption occurs for both probe molecules. The most striking feature in the spectra of these probe molecules is the very intense broad band in the $\nu(\equiv\text{CH})$ stretching region (see Figs. 4 and 5, and Table 2). The $\nu(\equiv\text{CH})$ band characterising adsorbed MA at 3268 cm^{-1} (see Fig. 4) is shifted by $-66\,cm^{-1}$ relative to the vapour phase band and has an FWHM of 140 cm^{-1} (see Table 2). The corresponding values for the $\nu(\equiv\text{CH})$ mode of the TA probe (band at 3255 cm^{-1}, Fig. 5) relative to the vapour phase band are −79 and 121 cm^{-1} (FWHM), respectively. Simultaneously, the $\nu(\text{C}\equiv\text{C})$ stretching mode near 2100 cm^{-1} is narrow with an FWHM of ca. 20 cm^{-1} and undergoes relatively small red-shifts of −17 and $-31\,cm^{-1}$ for MA and TA, respectively (see Table 2). These observations suggest that the acidic C–H groups are strongly perturbed by the adsorption interaction which is most likely described as a $\text{C–H}\cdots O^{2-}$ H-bonding interaction (Scheme 3). It must be noted, however, that the adsorbed molecules must also interact with the surface OH groups since the band of the unperturbed groups prior to adsorption are completely eroded on adsorption of MA or TA (see Figs. 4 and 5) with the simultaneous appearance of broad and complex bands at lower frequency. It is therefore inferred that the H-bonded molecules may simultaneously interact with OH groups in close proximity via π-bonding with the C≡C triple bond (Scheme 3). The complexity of these bands may arise from varying adsorption



Scheme 2. Model of the adsorption of TA on SiO_2.



Scheme 3. Model of the adsorption of MA and TA on MgO.

geometries and site configurations in the vicinity of the basic oxygen O^{2-}. It had been shown earlier [4] that methane only interacted with Mg^{2+} or O^{2-} corner sites at low temperature. It may thus be speculated that the basic O^{2-} centres which act as H-bond acceptor sites are located at corners and perhaps edges. Even the two substituted acetylenes may have sufficient freedom at these low-coordinated sites to undergo the additional π-bond interaction with neighbouring OH groups as suggested by the model in Scheme 3.

5. Conclusion

MA and TA physisorb on SiO_2 in analogous structures, which can be described as a π-interaction between the C≡C triple bond and the Brønsted acid silanol groups. On MgO, the physisorbed MA and TA perform strong interaction between their ≡CH group and the Lewis basic O^{2-} sites. This leads to a larger red-shift and a greater broadening of the ≡CH vibration mode for both MA and TA on MgO than on SiO_2. This means that a discrimination between acid and basic samples can be achieved by probing with MA and TA. Simultaneously to the $\equiv CH\cdots O^{2-}$ interaction on MgO an interaction occurs between the C≡C triple bond and OH groups preferably located near corner sites. The results suggest that the sterically more demanding TA molecule can still be adsorbed with analogous structures as MA (Scheme 3) probably because the preferred sites on the MgO surface are corner and perhaps edge sites. It is concluded that MA as well as TA can be used for discrimination between Brønsted acidic and Lewis basic sites and that a relative ranking of the basic strengths of series of catalyst materials may be obtained by FTIR spectroscopy of adsorbed MA and TA.

Acknowledgements

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