

# Adsorption of CH-acids on magnesia An FTIR-spectroscopic study

Sylvia Huber<sup>1</sup>, Helmut Knözinger<sup>\*</sup>

*Institut für Physikalische Chemie, Universität München, Sophienstrasse 11, 80333 Munich, Germany*

## Abstract

C–H acids including monofluoro-, trifluoro- and trichloromethane, as well as acetylene and methylacetylene were tested as probe molecules for basic sites on MgO by FTIR-spectroscopy. Adsorption structures, frequency shifts, and the applicability of various probes are discussed. Acetylene and methylacetylene undergo H-bonding interactions with Lewis-basic sites on the MgO surface. The experimental frequency shift of the CH-stretching modes can be taken as a measure of the strength of the basic sites. Two adsorption complexes are observed for trichloromethane (CHCl<sub>3</sub> and CCl<sub>3</sub>) with the CH- (CD-) mode being shifted to lower wavenumbers. A red shift of 36 cm<sup>-1</sup> was obtained for the H-bonded O<sup>2-</sup> ··· H–CCl<sub>3</sub>-complex. In contrast, the stronger CH-acid CF<sub>3</sub>H forms an adsorption complex in which hydrogen interacts with the basic oxygen sites and simultaneously one of the fluorine atoms is connected with a Mg<sup>2+</sup>-site. Adsorbed CH<sub>3</sub>F on MgO retains the C<sub>3v</sub>-symmetry and therefore, the most likely adsorption complex is Mg<sup>2+</sup> ··· F–CH<sub>3</sub>. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Adsorption; CH-acids; FTIR-spectroscopy; Magnesia; Basicity

## 1. Introduction

Extensive studies have been devoted to the characterization of solid acid catalysts over the last 30 years [1–4]. In contrast, less attention has been paid to basic properties and the characterization of basicity. To estimate the basic properties of a surface, two types of methodologies are used: titration with various reagents [5] and spectroscopic techniques [4,6–8]. Whereas the titration method only allows determination

of the total number of centres without differentiation of their properties, the use of spectroscopic techniques in conjunction with molecular probes, allows the nature and properties of basic centres to be studied.

The basic properties of oxide surfaces can be tested by acidic probe molecules combined with FTIR-spectroscopy. For this purpose these probe molecules must fulfil certain criteria [4]. In particular, a probe molecule should be unreactive relative to the surface to be characterized so that chemical transformations of the probe molecule cannot occur. It is for this reason that only very few acidic probe molecules for probing basic sites have been reported, and those mentioned in the literature are hardly ever universally ap-

<sup>\*</sup> Corresponding author. Fax: +49-89-590-2602

<sup>1</sup> Present address: BASF Aktiengesellschaft, Abt. ZAK/T, M325, 67056 Ludwigshafen, Germany.

plicable. A potentially useful class of probe molecules may be CH-acids. Paukshtis and Yurchenko [9] suggested trichloromethane as a probe molecule for basic centres. The adsorption of acetylene and methyl-substituted acetylenes on  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  was studied by Yates and Lucchesi [10]. Experiments using methane adsorption on MgO were reported by Li et al. [11] and Ferrari et al. [12]. Universally applicable probe molecules for the characterization of basic sites have not yet been found [7,8], largely because most of the probe molecules strongly interact with the surface, forming strong complexes, which can cause irreversible changes at the surface. In the present contribution, we have tested a series of CH-acidic molecules having distinct acid strength for their applicability as probe molecules. As a model basic solid, we used MgO. One group of probe molecules were trihalogeno methanes which are expected to undergo H-bonding interactions with  $\text{O}^{2-}$  acceptor sites. This should lead to low-frequency shifts of the isolated C–H stretching mode, which should be easy to detect and which should correlate with the H-bond acceptor strength of the  $\text{O}^{2-}$  site. The isolated C–H stretching mode of methylacetylene should be analogously affected and was thus included into this study. Unsubstituted acetylene was also studied because of its high symmetry which is expected to be reduced by the adsorption interaction and provide interesting information on adsorption geometries.

## 2. Experimental

The probe molecules acetylene (5% in He) and methylacetylene ( $\geq 99.5\%$ ) were obtained from Linde; trichloromethane ( $> 99\%$ ) and trifluoromethane ( $\geq 98\%$ ) were from Merck and monofluoromethane ( $> 98.5\%$ ) from Euriso-Top.

MgO was prepared as described by Kirilin et al. [13] and the specific surface area of this material ( $35 \text{ m}^2/\text{g}$ ) was determined by nitrogen

adsorption. For FTIR-spectroscopy, self-supporting wafers were pressed with a pressure of 15 MPa for 10 min. The resulting wafers ( $15 \text{ mg}/\text{cm}^2$ ) were pretreated in situ in an oxygen flow at 773 K for 1 h, followed by evacuation ( $\sim 10^{-3} \text{ Pa}$ ) at 773 K for 1 h. Prior to admission of trifluoromethane and monofluoromethane, the wafer was cooled with liquid nitrogen to 150 K. Adsorption of acetylene, methylacetylene, and trichloromethane was carried out at room temperature.

IR transmission spectra were recorded using a Bruker IFS66 FTIR-spectrometer, with a spectral resolution of  $0.7 \text{ cm}^{-1}$  as a function of equilibrium pressure of the adsorbate. A total of 256 scans were accumulated. A detailed description of the low-temperature transmission cell, which was used for adsorption of the halogenated compounds, has been reported previously [14]. For adsorption of acetylene and its derivatives, a stainless steel transmission cell provided by ISRI (In situ Research and Instruments, South Bend, USA) was used.

## 3. Results and discussion

### 3.1. Adsorption of chlorinated and fluorinated methane

Halogenated methanes such as trichloromethane and trifluoromethane, are considered as suitable probes for FTIR-spectroscopic characterization of basic sites on oxides and in zeolites. The C–H-stretching mode shifts to lower frequencies relative to the gas phase if an  $\text{O}^{x-} \cdots \text{H}-\text{C}$ -interaction can be detected. The normal modes of the gaseous compounds are given in Table 1, for comparison purposes.

#### 3.1.1. Adsorption of $\text{CDCl}_3$ and $\text{CHCl}_3$

Fig. 1 shows the FTIR-spectra of  $\text{CHCl}_3$  adsorbed on MgO at 290 K. Two bands are observed in the symmetric CH-stretching region of adsorbed  $\text{CHCl}_3$  at 3011 and  $2983 \text{ cm}^{-1}$ . The HCCl-mode ( $\nu_4$ ) gives also rise to two

Table 1  
Normal modes [in  $\text{cm}^{-1}$ ] of  $\text{CHCl}_3$  [15,16]  $\text{CDCl}_3$  [17],  $\text{CHF}_3$  [18,19] and  $\text{CH}_3\text{F}$  [20]

	$\nu_1$ ( $a_1$ )	$\nu_2$ ( $a_1$ )	$\nu_3$ ( $a_1$ )	$\nu_4$ (e)	$\nu_5$ (e)	$\nu_6$ (e)
$\text{CHCl}_3$	3019	668	366	1216	761	262
$\text{CDCl}_3$	2253	651	366	908	738	262
$\text{CHF}_3$	3035	1209	700	1377	1152	508
$\text{CH}_3\text{F}$	2965	1475	1048	2982	1471	1196

bands at 1240 and  $1216 \text{ cm}^{-1}$ . If the  $\text{C}_{3v}$ -symmetry of the trichloromethane is lowered to  $\text{C}_{2v}$  or  $\text{C}_s$ , the doubly degenerate  $\nu_4$  mode is expected to split into two components. However, there is no linear correlation of the integral intensities of the bands at 1240 and  $1216 \text{ cm}^{-1}$  at different partial pressures. Therefore, it can be concluded that two different kinds of adsorption species are formed with  $\text{CHCl}_3$ . For determination of integral intensities the overlapping bands were deconvoluted as shown in Fig. 1. Fig. 2 shows the correlation of the integral intensities of  $\nu_1$  and  $\nu_4$  modes of adsorbed  $\text{CHCl}_3$ . The integral intensities of the band at  $3011 \text{ cm}^{-1}$  at various pressures of  $\text{CHCl}_3$  and the integral intensities of the band at  $1240 \text{ cm}^{-1}$ , as well as those of the bands at  $2983 \text{ cm}^{-1}$  and at  $1216 \text{ cm}^{-1}$ , show a linear correlation. This supports the conclusion that the bands at  $3011$  and  $1240 \text{ cm}^{-1}$ , and the bands at  $2983$  and  $1216 \text{ cm}^{-1}$ , respectively, are caused by two different kinds of adsorption species.

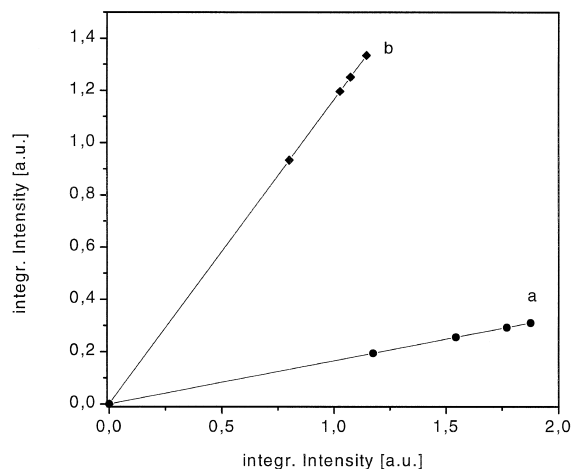


Fig. 2. Adsorption of  $\text{CHCl}_3$  on  $\text{MgO}$ : (a) Correlation of the integral intensities of bands at  $1216$  and  $2983 \text{ cm}^{-1}$ , (b) Correlation of the integral intensities of bands at  $1240$  and  $3011 \text{ cm}^{-1}$ .

These results can be further supported by the adsorption of  $\text{CDCl}_3$ . Adsorption of  $\text{CDCl}_3$  reveals bands at  $2245$  and  $2220 \text{ cm}^{-1}$ , which correspond to a red shift of  $8$  and  $33 \text{ cm}^{-1}$ , respectively, as compared to the gas phase spectrum. The C–H and C–D frequency ratios are in good agreement with the calculated value of  $1.34$ .

These observations are in agreement with results reported by Paukshtis and Yurchenko [9] and Paukshtis et al. [21,22], who studied the adsorption of trichloromethane on different ox-

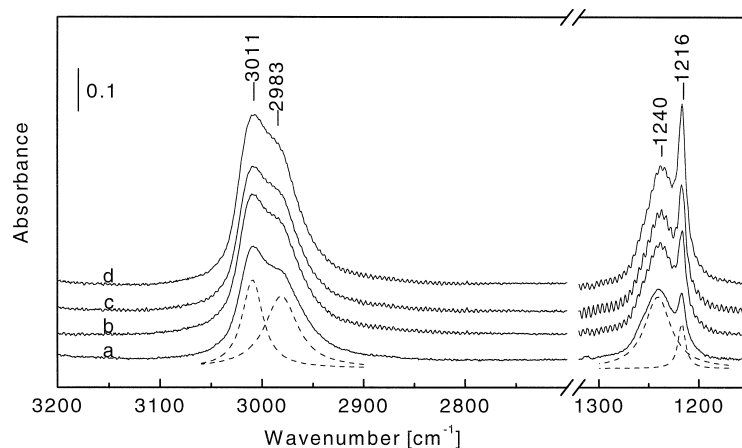


Fig. 1. FTIR-spectra of the adsorption of (a)  $0.05$ , (b)  $0.07$ , (c)  $0.1$  and (d)  $0.15 \text{ kPa}$   $\text{CHCl}_3$  on  $\text{MgO}$  at  $290 \text{ K}$ .

ides. They observed two bands at 3010 and 2960  $\text{cm}^{-1}$  for the CH-stretching mode of  $\text{CHCl}_3$  adsorbed on MgO (2245 and 2210  $\text{cm}^{-1}$  for the CD-stretching mode of adsorbed  $\text{CDCl}_3$ ). Fig. 3 shows possible interactions of trichloromethane with Lewis-acidic and Lewis-basic sites. The large half width of the CH- (as well as the half width of the CD-) stretching mode at 3011  $\text{cm}^{-1}$  (or 2245  $\text{cm}^{-1}$ ) indicates an  $\text{O}^{2-} \cdots \text{H(D)}-\text{CCl}_3$  interaction. The half width of the lower frequency band at 2983  $\text{cm}^{-1}$  is approximately  $1.8 \times$  broader when compared with the band at 3011  $\text{cm}^{-1}$ . A stronger red shift is expected for an only acid–base interaction (complex I) than for a complex in which the chlorine atom and the hydrogen atom interact with both the Lewis-acid and the Lewis-basic sites simultaneously (complex II). A frequency shift to higher wavenumbers is expected if only the chlorine atom interacts with Lewis-acid sites (complex III), because in this case the C–H(D)-bond becomes stronger.

In agreement with Paukshtis and Yurchenko [9] and Paukshtis et al. [21,22] and Xie et al. [23], the band at 2983  $\text{cm}^{-1}$  is attributed to complex I of adsorbed  $\text{CHCl}_3$  (at 2220  $\text{cm}^{-1}$  for adsorbed  $\text{CDCl}_3$ ), while the higher frequency band is connected with complex II. However, a symmetry reduction of adsorbed trichloromethane should lead to a splitting of the  $\nu_4$ -mode into two components. This suggests that the splitting is probably too small to be resolved in these spectra but presumably led to significant line broadening. The OH-stretching vibration at 3750  $\text{cm}^{-1}$  shows no shift. There-

fore an interaction of trichloromethane with the OH-groups of MgO, as discussed by Davydov et al. [24], is not observed.

Two adsorption complexes are observed for  $\text{CHCl}_3$  (or  $\text{CDCl}_3$ ) with the C–H- (C–D-) mode being shifted to lower wavenumbers. A red shift of 36  $\text{cm}^{-1}$  (33  $\text{cm}^{-1}$ ) was obtained for the H-bonded  $\text{O}^{2-} \cdots \text{H(D)}-\text{CCl}_3$ . Kustov et al. [25] reported shifts to lower frequencies between 15 and 110  $\text{cm}^{-1}$  for  $\text{MgO}/\text{Al}_2\text{O}_3$  and  $\text{K}_2\text{CO}_3/\text{Al}_2\text{O}_3$ . Gordymova and Davydov [26] observed, besides the CH- or the CD-stretching mode, bands at about 1600 and 1390  $\text{cm}^{-1}$  on  $\gamma$ -alumina which they assigned to formate species. These bands were not observed in the present work on MgO.

### 3.1.2. Adsorption of $\text{CHF}_3$ and $\text{CH}_3\text{F}$

The use of the stronger CH-acid  $\text{CHF}_3$  should also lead to a red shift of the CH-stretching mode if it forms an H-bonded complex. As shown in Fig. 4,  $\text{CHF}_3$  adsorbed at 150 K on MgO gives rise to the following IR-bands: the very weak  $\nu_1$ -mode is observed at 3055  $\text{cm}^{-1}$ , the  $\nu_2$ -mode at 1200  $\text{cm}^{-1}$ , the doubly degenerate  $\nu_4$ -mode at 1375  $\text{cm}^{-1}$ , and in the CF-region there are two bands at 1158 and 1116  $\text{cm}^{-1}$ .  $\text{CHF}_3$  can be removed by warming up to room temperature. Contrary to expectations, the  $\nu_1$ -mode shifts to higher frequencies. Fig. 5 shows possible interactions of  $\text{CHF}_3$  with MgO. Complex I should lead to a red shift of the  $\nu_1$ -mode because of the weakening of the C–H-bond. Therefore, it can be concluded that the fluorine atoms must be involved in the interactions with

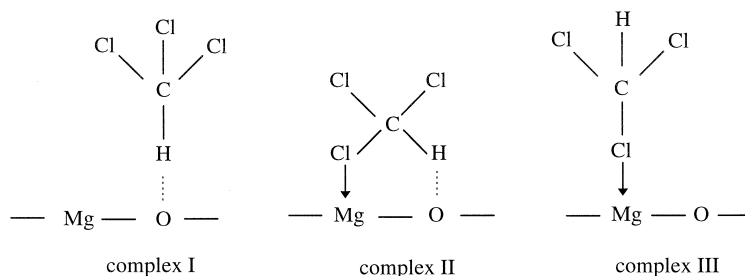


Fig. 3. Possible interactions of  $\text{CHCl}_3$  with MgO.

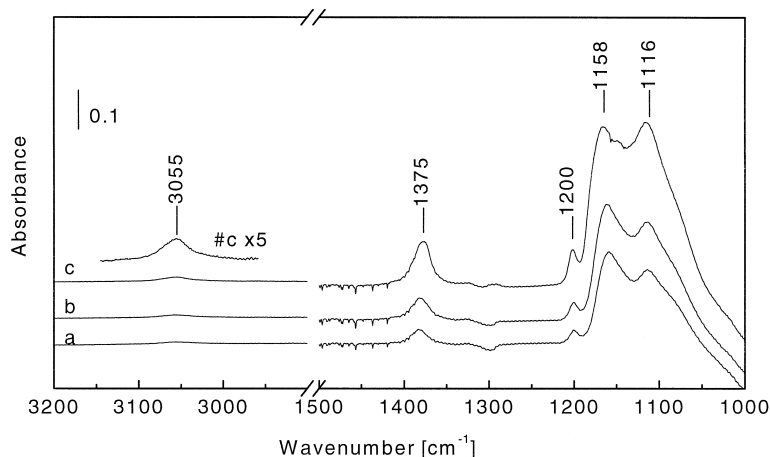


Fig. 4. FTIR-spectra of the adsorption of (a) 0.01, (b) 0.05 and (c) 0.1 kPa  $\text{CHF}_3$  on MgO at 150 K.

MgO. The large half width of the  $\nu_1$ -mode ( $45 \text{ cm}^{-1}$  at 0.05 kPa  $\text{CHF}_3$ ) suggests that the C–H-bond is directly involved in the adsorption interaction. These results lead to the conclusion that the stronger CH-acid  $\text{CF}_3\text{H}$  forms an adsorption complex in which the hydrogen interacts with a basic oxygen site, while one of the fluorine atoms is simultaneously connected with a  $\text{Mg}^{2+}$ -site (Fig. 5, complex V).

$\text{CHF}_3$  and  $\text{CHCl}_3$  belong to the point group  $\text{C}_{3v}$ , and the symmetry reduction of  $\text{C}_{3v}$  to  $\text{C}_s$ , as in the proposed complex, should lead to a splitting of the doubly degenerate modes  $\nu_4$ ,  $\nu_5$  and  $\nu_6$ . Due to the extremely low transmittance of the  $\text{CaF}_2$  windows in the IR-transmission cell below  $1000 \text{ cm}^{-1}$ , the  $\nu_3$ - and the  $\nu_6$ -mode cannot be observed in the spectra. The detected broad and intense bands in the CF-region ( $\nu_5$ -mode) at 1158 and  $1116 \text{ cm}^{-1}$  indicate the symmetry reduction. The splitting of the  $\nu_4$ -

mode cannot be resolved in the spectra, but may be responsible for the large width of the band at  $1375 \text{ cm}^{-1}$ .

Adsorption of  $\text{CH}_3\text{F}$  on MgO was carried out to study the interaction between fluorinated compounds and Lewis-acidic and basic sites (Fig. 6). The  $\nu_1$ -band is observed at  $2966 \text{ cm}^{-1}$ , which is near the frequency of gaseous  $\text{CH}_3\text{F}$ . The  $\nu_2$ - and the  $\nu_5$ -modes can be seen at 1470 and  $1454 \text{ cm}^{-1}$  (not shown) and the first overtone of these bands is observed at 2860 and  $2850 \text{ cm}^{-1}$ . The band at  $3019 \text{ cm}^{-1}$  can be assigned to the doubly degenerate  $\nu_4$ -mode which has a large width but does not show splitting. In comparison to the adsorption of  $\text{CHF}_3$  the half width of this band is smaller ( $25 \text{ cm}^{-1}$  at 0.03 kPa  $\text{CH}_3\text{F}$ ), which probably excludes an  $\text{O}^{2-} \cdots \text{H}-\text{CH}_2\text{F}$ -complex. The doubly degenerate  $\nu_6$ -mode is observed with low intensity at  $1177 \text{ cm}^{-1}$ .

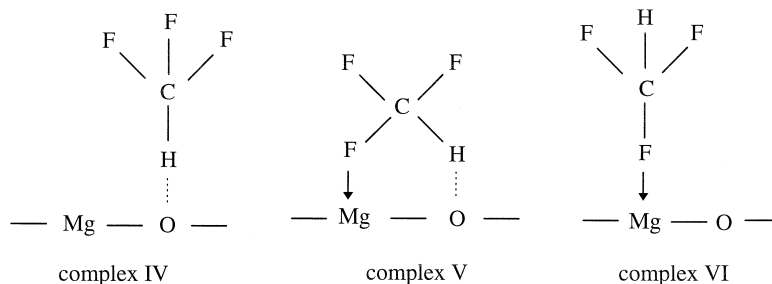


Fig. 5. Possible interactions of  $\text{CHF}_3$  with MgO.

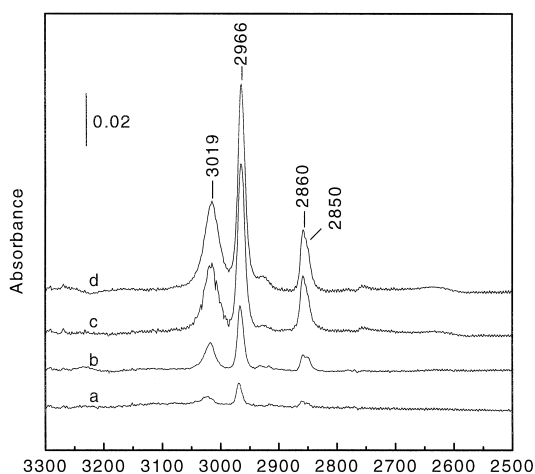


Fig. 6. FTIR-spectra of the adsorption of (a) 0.01, (b) 0.03, (c) 0.1 and (d) 0.5 kPa  $\text{CH}_3\text{F}$  on MgO at 150 K.

These results lead to the conclusion that the  $\text{C}_{3v}$  symmetry of  $\text{CH}_3\text{F}$  is retained when the molecule is adsorbed on MgO. Compared to the assignment of Heidberg et al. [27], who studied the adsorption of  $\text{CH}_3\text{F}$  on NaCl and proposed a  $\text{Na}^+ \cdots \text{F}-\text{CH}_3$ -complex, the most likely adsorption complex on MgO is thus  $\text{Mg}^{2+} \cdots \text{F}-\text{CH}_3$ .

Neither  $\text{CHF}_3$ , nor the weaker CH-acid  $\text{CH}_3\text{F}$ , show a red shift of the CH-stretching mode. In contrast to  $\text{CHCl}_3$  ( $\text{CDCl}_3$ ), fluorinated methane cannot be used as a direct measure of the basic strength of oxides, because of its complex type of adsorption interaction but it may provide information on properties of acid–base pair sites.

### 3.2. Adsorption of acetylene and derivatives

Acetylene and monosubstituted acetylenes are C–H acids and should undergo  $\text{O}^{2-} \cdots \text{H}-\text{C}\equiv\text{C}-\text{R}$  H-bonding interactions with basic oxygen centres on oxide surfaces, which are expected to induce a red shift of the C–H stretching mode depending on the strength of the H-bond and hence, on the acceptor or basic strength of the  $\text{O}^{2-}$  site. The normal modes of gaseous  $\text{C}_2\text{H}_2$  and  $\text{CH}_3-\text{C}\equiv\text{C}-\text{H}$  (or  $\text{CH}_3-\text{C}\equiv\text{C}-\text{D}$ ) are given in Tables 2 and 3, respectively.

Table 2  
Normal modes [in  $\text{cm}^{-1}$ ] of  $\text{C}_2\text{H}_2$  [28]

	$\nu_1$	$\nu_2$	$\nu_3$	$\nu_4$	$\nu_5$
$\text{C}_2\text{H}_2$	3373 (R)	1974 (R)	3287 (IR)	612 (R)	729 (IR)

Adsorption of acetylene at 280 K reveals a broad asymmetric band at  $3150 \text{ cm}^{-1}$  (Fig. 7). The appearance of rotation structure at  $3287 \text{ cm}^{-1}$  at a pressure of 0.025 kPa  $\text{C}_2\text{H}_2$  indicates the presence of gaseous acetylene (Fig. 7 spectrum (f)). The adsorption leads to a shift of the antisymmetric CH-stretching mode ( $\nu_3$ ) to lower frequency by  $137 \text{ cm}^{-1}$  indicative of H-bonding, and the asymmetric shape of this broad band indicates an interaction with sites of variable acceptor strength. The IR silent  $\nu_2$ -mode becomes activated and appears at  $1942 \text{ cm}^{-1}$ . Adsorbed acetylene can be removed by evacuation at room temperature. The appearance of the  $\nu_2$ -mode and the red shift of the  $\nu_3$ -mode are clear evidence for an H-bonded complex:  $\text{O}^{2-} \cdots \text{H}-\text{C}\equiv\text{CH}$ .

By analogy to the IR-silent  $\nu_2$ -mode, the symmetric CH-stretching mode ( $\nu_1$ ) should also be activated although it may be weak. The Raman frequency of the  $\nu_1$ -mode of gaseous acetylene is located at  $3373 \text{ cm}^{-1}$ . As shown in Fig. 7, the symmetric CH-stretching mode is probably superimposed by the  $\nu_3$  gas phase bands. The adsorption induced symmetry reduction of the  $\text{C}_2\text{H}_2$  makes the two C–H-bonds

Table 3  
Normal modes [in  $\text{cm}^{-1}$ ] of  $\text{CH}_3-\text{C}\equiv\text{C}-\text{H}$  and  $\text{CH}_3-\text{C}\equiv\text{C}-\text{D}$  [28,29]

	$\text{C}_3\text{H}_4$	$\text{C}_3\text{H}_3\text{D}$
$\nu_1$ CH(D) ( $a_1$ , IR/R)	3334	2674
$\nu_2$ CH ( $a_1$ , R)	2941	2941
$\nu_3$ C≡C ( $a_1$ , IR/R)	2142	2009
$\nu_4$ $\text{CH}_3$ ( $a_1$ , IR/R)	1383	1376
$\nu_5$ C–C ( $a_1$ , IR/R)	926	914
$\nu_6$ CH ( $e$ , IR/R)	3008	3009
$\nu_7$ $\text{CH}_3$ ( $e$ , IR/R)	1448	1454
$\nu_8$ $\text{CH}_3$ ( $e$ , IR/R)	1041	1037
$\nu_9$ C≡C–H(D) ( $e$ , IR/R)	643	498
$\nu_{10}$ C–C≡C ( $e$ , R)	336	314

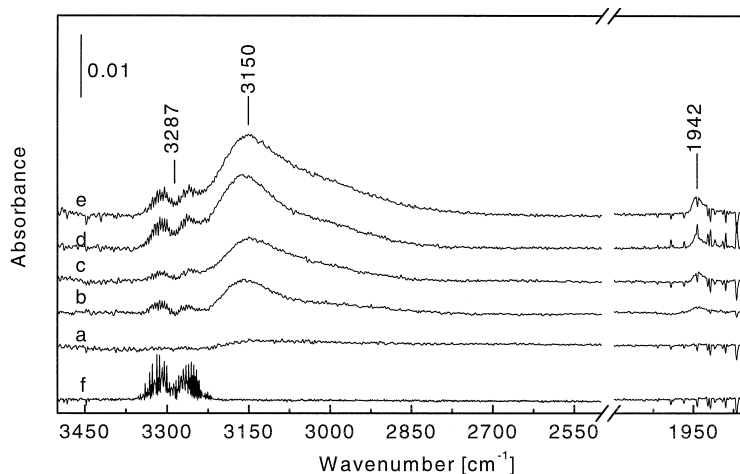


Fig. 7. FTIR-spectra of the adsorption of (a) 0.005, (b) 0.025, (c) 0.1, (d) 0.25 kPa, (e) 0.5 kPa of adsorbed  $C_2H_2$  on MgO at 290 K and (f) 0.15 kPa gaseous  $C_2H_2$ .

inequivalent. Therefore, in the spectra of adsorbed  $C_2H_2$ , there should be two bands for the antisymmetric stretching ( $\nu_3^-$ ) mode. Due to the fact that the antisymmetric stretching vibration appears as a very broad and asymmetric band (half width of the  $\nu_3^-$ -mode more than  $100\text{ cm}^{-1}$ ) there cannot be observed a clear splitting of this band.

Yates and Lucchesi [10] observed two different adsorption complexes with acetylene on  $Al_2O_3$  and  $SiO_2$ . The strongly-held acetylene was thought to be orientated perpendicular to the surface and displayed bands at 3300 and

$2007\text{ cm}^{-1}$ , while the weakly-held acetylene was thought to be adsorbed parallel to the surface and bands at 3220 and  $1950\text{ cm}^{-1}$  could be observed. The authors assigned the bands of the stronger adsorbed species to a  $Su \cdots C \equiv C-H$  complex (where Su represents a surface atom), and the weaker adsorbed species to an interaction of the Lewis-acid sites with the  $\pi$ -electrons of the triple bond. Because of the ease of desorption of acetylene from MgO, dissociation appears to be unlikely.

These conclusions are further supported by the coadsorption of  $C_2H_2$  and  $CDCl_3$  (Fig. 8).

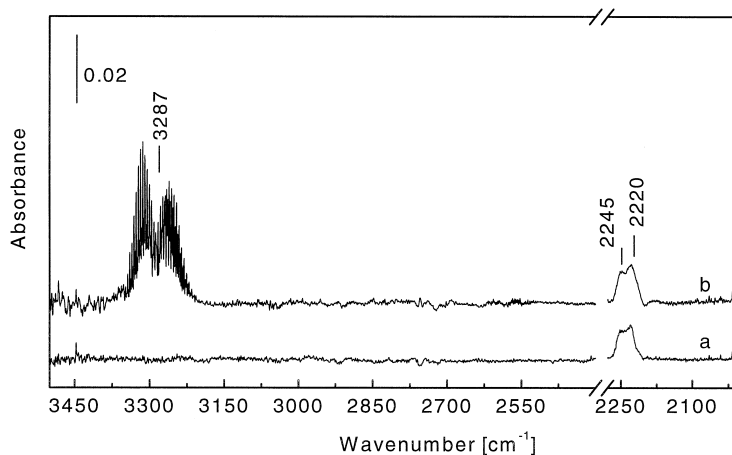


Fig. 8. FTIR-spectra of the adsorption of (a) 0.01 kPa  $CDCl_3$  and (b) 1 kPa  $CDCl_3$  + 2 kPa  $C_2H_2$  on MgO at 290 K.

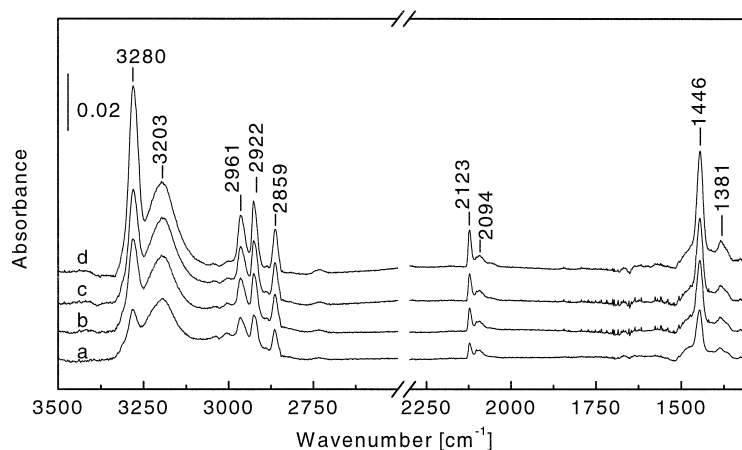


Fig. 9. FTIR-spectra of the adsorption of (a) 0.02, (b) 0.05, (c) 0.07 and (d) 0.1 kPa  $C_3H_4$  on MgO at 290 K.

As described in Section 3.1.1., adsorption of  $CDCl_3$  at room temperature reveals bands at 2245 and 2220  $cm^{-1}$  (Fig. 8 spectrum (a)), where the adsorption sites for  $CDCl_3$  are mainly the Lewis-basic sites. Fig. 8 spectrum (b) shows the IR-spectrum after exposure of MgO to 1 kPa  $CDCl_3$  and 2 kPa  $C_2H_2$ . Besides the bands of adsorbed  $CDCl_3$  only gaseous  $C_2H_2$  can be seen; no band of adsorbed acetylene is observed. This indicates that the Lewis-basic sites are already occupied by the trichloromethane molecules.

The substitution of one hydrogen atom of acetylene by a methyl group leads to the weaker CH-acid,  $CH_3-C\equiv C-H$ . In contrast to acetylene, the adsorption of methylacetylene produces two bands at 3280 and 3203  $cm^{-1}$  for the  $\nu_1$ -mode (Fig. 9). The half width of the lower frequency band is approximately twice the half width of the higher frequency band. For the  $\nu_3$ -mode, also two bands are observed at 2123 and 2094  $cm^{-1}$ . The band at 2961  $cm^{-1}$  can be assigned to the doubly degenerate  $\nu_6$ -mode, and the band at 2922  $cm^{-1}$  can be attributed to the  $\nu_2$ -mode. The  $\nu_7$ - and the  $\nu_4$ -modes are observed at 1446 and 1381  $cm^{-1}$ , and the first overtone of  $\nu_7$  can be seen at 2859  $cm^{-1}$ .

Fig. 10 shows possible complexes between the methylacetylene and the surface of MgO. The two observed bands for the non-degenerate

$\nu_1$ -, as well as for the  $\nu_3$ -mode, are clear evidence that methylacetylene adsorbs in two different adsorption geometries. On one hand, methylacetylene may be attached perpendicularly to the surface via its acetylenic end (Fig. 10 complex VII) and on the other hand, it may be oriented parallel to the surface (Fig. 10 complex VIII). Both pairs of  $\nu_1$ - and  $\nu_3$ -modes undergo a red shift on adsorption which appears to be consistent with the proposed adsorption species. The band at 3203  $cm^{-1}$  is shifted relative to the  $\nu_1$ -mode of the free molecule (3334  $cm^{-1}$ ) by  $-131 cm^{-1}$  and the band width is significantly increased. Therefore, this band can most likely be attributed to an H-bonded complex VII (Fig. 10). The corresponding  $\nu_3$ -mode is most probably the band at 2094

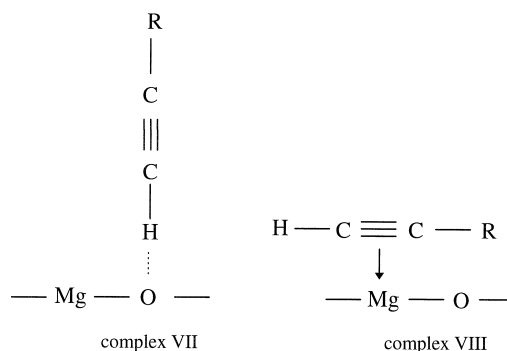


Fig. 10. Possible interactions of  $HC\equiv CR$  with MgO ( $R=CH_3$ ).



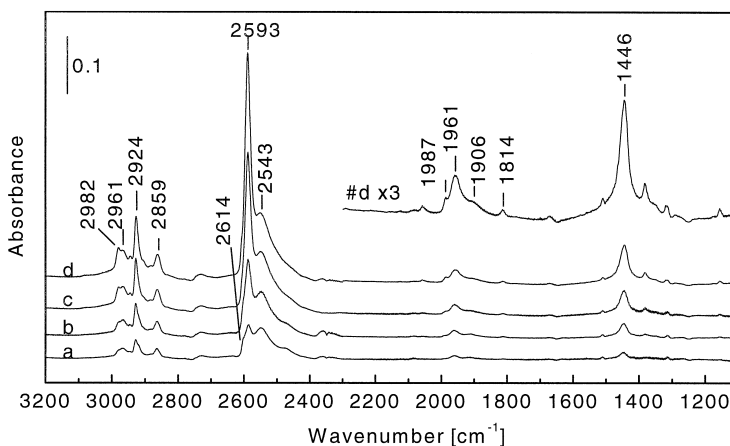


Fig. 11. FTIR-spectra of the adsorption of (a) 0.05, (b) 0.1, (c) 0.5 and (d) 1 kPa  $\text{CH}_3\text{-C}\equiv\text{C-D}$  on MgO at 290 K.

$\text{cm}^{-1}$ , since the intensity of this bands seems to correlate with that of the  $\nu_1$ -mode at  $3203 \text{ cm}^{-1}$ . Both bands saturate at low equilibrium pressures, while the intensities of the second pair of bands at  $3280$  and  $2123 \text{ cm}^{-1}$  continuously grow as the pressure increases within the covered range. These bands are therefore attributed to a more weakly adsorbed species, most likely the  $\pi$ -complex VIII (Fig. 10). It is inferred that the H-bonded complex is strongly preferred for acetylene because of its higher acidity so that the  $\pi$ -complex formation plays a negligible role and remains undetected within the covered pressure range.

These band assignments are supported by the spectra recorded after adsorption of deuterated methylacetylene  $\text{CH}_3\text{C}\equiv\text{CD}$ . Fig. 11 shows the FTIR-spectra after exposure of MgO to  $\text{C}_3\text{H}_3\text{D}$  with the assignments of the observed frequencies given in Table 4. The two bands in the  $\nu_1$ -region at  $2593$  and  $2543 \text{ cm}^{-1}$  correspond to the bands observed at  $3280$  and  $3203 \text{ cm}^{-1}$ , respectively, for adsorbed  $\text{CH}_3\text{C}\equiv\text{C-H}$  (Fig. 9). The  $\nu_1(\text{C-H})/\nu_1(\text{C-D})$  frequency ratios are 1.26. At low pressures a very weak band can be detected at  $2614 \text{ cm}^{-1}$  which is superimposed by the strong band at  $2593 \text{ cm}^{-1}$  at higher pressures. The width at half maximum of the band at lower frequency, namely  $2543 \text{ cm}^{-1}$  is approximately twice as large as that of the band

at  $2593 \text{ cm}^{-1}$ . This compares nicely with the relative band widths of the two  $\nu_1$ -modes in the C–H stretching region observed for the hydrogen form of methylacetylene. These observations are consistent with the attribution of the high and low frequency components in the  $\nu_1$ -region to the  $\pi$ -complex VIII and the H-bonded species VII, respectively. The calculated frequency shift for the H-bonded complex in the C–D region is  $131 \text{ cm}^{-1}$  and is identical to the shift seen in the C–H region for adsorbed  $\text{CH}_3\text{C}\equiv\text{C-H}$ .

The  $\nu_3$ -modes of the adsorbed deuterated methylacetylene are also shifted to lower frequencies and appear around  $1960 \text{ cm}^{-1}$  in Fig. 11. Additional weak bands at  $1906$ ,  $1814$  and between  $1510$  and  $1150 \text{ cm}^{-1}$  can be assigned to combination bands and overtones.

The weak band which can be seen at  $2614 \text{ cm}^{-1}$  at low pressures may be tentatively attributed to a second  $\pi$ -complex being formed at low abundance.

Table 4  
Frequencies [in  $\text{cm}^{-1}$ ] of adsorbed  $\text{C}_3\text{H}_3\text{D}$  on MgO

$\nu_1$	$\nu_2$	$\nu_3$	$\nu_4$	$\nu_6$	$\nu_7 (2\nu_7)$
2614	2924	1987	1381	2982	1446
2593	$\sim 2920^{\text{(sh)}}$	1961		2961	(2859)
2543					

sh: shoulder.

#### 4. Conclusions

Acetylene, methyl acetylene, and trichloromethane undergo H-bonding interactions with basic  $O^{2-}$ -sites on the MgO surface.

The experimental frequency shifts of the CH- and CD-stretching modes of halogenated compounds are summarized in Table 5. A completely different behavior was obtained for chlorinated and fluorinated methane. In contrast to chlorine atoms fluorine atoms do not produce an M-effect but their inductive effect is particularly strong. The high electronegativity (EN: 4.1) and the smaller size of the fluorine atoms as compared to the chlorine atoms, favors the additional interaction with Lewis-acid sites via a F-atom as exemplified by complex V in Fig. 5. A simple H-bonding interaction is only observed for the adsorption of trichloromethane. Therefore, fluorine substituted methanes cannot generally be used as probe molecules to study the basicity of oxides, although they may provide information on properties of acid–base pair sites. The moderate acidity of trichloromethane allows it to be used as a probe for sites of different basic strength. Although two different kinds of adsorption geometries are observed for trichloromethane adsorbed on MgO, both species are well-resolved and the CH-stretching mode of the  $O^{2-} \cdots H-C$ -complex can be easily assigned.

The experimental CH-, CD- and CC-stretching modes and the shifts of adsorbed acetylene and methylacetylene on MgO are summarized in Table 6. The red shifts of the CH-stretching

Table 5

CH-, CD-frequencies and the shift ( $\Delta\nu_{CH \text{ or } CD}$ ) [in  $cm^{-1}$ ] of adsorbed halogenated methanes on MgO

	$\nu_{CH \text{ or } CD}$	$\Delta\nu_{CH \text{ or } CD}$
CHCl <sub>3</sub>	2983	−36
	3011	−8
CDCl <sub>3</sub>	2220	−33
	2245	−8
CHF <sub>3</sub>	3055	+20
CH <sub>3</sub> F	3019	+37

Table 6

CH-, CD- and CC-frequencies and the shifts ( $\Delta\nu_{CH \text{ or } CD}$  and  $\Delta\nu_{CC}$ ) [in  $cm^{-1}$ ] of adsorbed acetylene and methylacetylene ( $CH_3-C\equiv C-H$  and  $CH_3-C\equiv C-D$ ) on MgO

	$\nu_{CH \text{ or } CD}$	$\Delta\nu_{CH \text{ or } CD}$	$\nu_{CC}$	$\Delta\nu_{CC}$
C <sub>2</sub> H <sub>2</sub>	3150	−137	1942	−32
C <sub>3</sub> H <sub>4</sub>	3280	−54	2123	−19
	3203	−131	2094	−48
C <sub>3</sub> H <sub>3</sub> D	2614	−60	1987	−22
	2593	−81	1961	−48
	2543	−131		

modes show that acetylene and methylacetylene offer favorable properties for the characterization of the basic sites. Methylacetylene forms two adsorption complexes. However, the band splitting for both species is well-resolved allowing a clear distinction.

Therefore, we can conclude that the experimental frequency shifts of trichloromethane, acetylene and methylacetylene, can be taken as a measure of the base strength of adsorption sites. In contrast, fluorine-substituted methanes are less suitable as probe molecules because of their strong additional interactions with Lewis-acid sites via the fluorine atoms. The application of acetylene as a probe molecule may be limited to relatively strong solid bases because otherwise polymerization of acetylene may take place.

It should also be mentioned that a theoretical study of the low temperature adsorption of methane using density functional techniques [12] has recently shown that this molecule only interacts with edge and corner sites, but not on the (100) plane. The location of the  $O^{2-}$  sites for adsorption of trichloromethane and acetylenes is not clear at this time but a study into this problem is presently under way.

#### Acknowledgements

This work was carried out in the framework of a Sonderforschungsbereich SFB 338 and it was financially supported by the Deutsche Forschungsgemeinschaft, the Bundesminister für

Bildung und Forschung and by the Fonds der Chemischen Industrie.

## References

- [1] D. Barthomeuf, *Mater. Chem. Phys.* 17 (1987) 49.
- [2] H. Knözinger, in: R.W. Joyner, R.A. Van Santen (Eds.), *Elementary Reaction Steps in Heterogeneous Catalysis*, Kluwer Academic Publ., Dordrecht, 1993, p. 267.
- [3] J.A. Lercher, C. Gründling, G. Eder-Mirth, *Catal. Today* 27 (1996) 353.
- [4] H. Knözinger, in: G. Ertl, H. Knözinger, J. Weitkamp (Eds.), *Handbook of Heterogeneous Catalysis*, Vol. 2, Wiley, Weinheim, 1997, p. 707.
- [5] K. Tanabe, M. Misono, Y. Ono, H. Hattori, in: B. Delmon, J.T. Yates (Eds.), *New Solid Acids and Bases—Their Catalytic Properties*, *Stud. Surf. Sci. Catal.* Vol. 51, Kodansha, Tokyo, 1989.
- [6] D. Barthomeuf, G. Coudurier, J.C. Vedrine, *Mater. Chem. Phys.* 18 (1988) 553.
- [7] J.C. Lavalley, *Catal. Today* 27 (1996) 377.
- [8] J.C. Lavalley, *Trends Phys. Chem.* 2 (1991) 305.
- [9] E.A. Paukshtis, E.N. Yurchenko, *Russ. Chem. Rev.* 52 (1983) 242.
- [10] D.J.C. Yates, P.J. Lucchesi, *J. Chem. Phys.* 35 (1961) 243.
- [11] C. Li, G. Li, Q. Xin, *J. Phys. Chem.* 1994 (1993) 98.
- [12] A.M. Ferrari, S. Huber, H. Knözinger, K.M. Neyman, N. Rösch, *J. Phys. Chem. B* 102 (1998) 4548.
- [13] P.S. Kirlin, H. Knözinger, B.C. Gates, *J. Phys. Chem.* 94 (1990) 8451.
- [14] G. Kunzmann, PhD Thesis, University of Munich, Germany, 1987.
- [15] S. Bahagavantam, *Phys. Rev.* 53 (1938) 1015.
- [16] J. Weidlein, U. Müller, K. Dehnike, *Schwingungsfrequenzen/Band I and II*, Georg Thieme Verlag, Stuttgart, New York, 1981.
- [17] R.W. Wood, D.H. Rank, *Phys. Rev.* 48 (1935) 63.
- [18] H.J. Bernstein, G. Herzberg, *J. Phys. Chem.* 16 (1948) 30.
- [19] C.C. Costain, *J. Mol. Spectr.* 9 (1962) 317.
- [20] W.L. Smith, J.M. Mills, *J. Mol. Spectr.* 11 (1963) 11.
- [21] E.A. Paukshtis, N.S. Kotsarenko, L.G. Karakchiev, *React. Kinet. Catal. Lett.* 12 (1979) 315.
- [22] E.A. Paukshtis, P.I. Soltanov, E.N. Yurchenko, K. Jiratova, *Collect. Czech. Chem. Commun.* 47 (1982) 2044.
- [23] J. Xie, M. Huang, S. Kaliaguine, *React. Kinet. Catal. Lett.* 58 (1996) 217.
- [24] A.A. Davydov, M.L. Shepótko, A.A. Budneva, *Kinet. Catal.* 35 (1994) 272.
- [25] L.M. Kustov, E.B. Uvarova, V.B. Kazansky, F. Figueras, D. Tichit, *Europacat-II*, Maastricht, Book of Abstracts, 1995, p. 395.
- [26] D.A. Gordymova, A.A. Davydov, *React. Kinet. Lett.* 23 (1983) 233.
- [27] J. Heidberg, I. Hussla, Z. Szilagyi, *J. Electr. Spectr. Rel. Phen.* 30 (1983) 53.
- [28] G. Herzberg, *Molecular Spectra and Molecular Structure: II. Infrared and Raman Spectra of Polyatomic Molecules*, Van Nostrand Reinhold, New York, 1945.
- [29] R.J. Grisenthwaite, H.W. Thompson, *Trans. Faraday Soc.* 50 (1954) 212.