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IR Study of Acetonitrile Adsorption on Hydroxylated Zirconium Dioxide: Mechanism of Acetonitrile Hydrolysis

Abdelakrim Aboulayt, Claude Binet* and Jean-Claude Lavalley
Laboratoire Catalyse et Spectrochimie—URA CNRS 414 ISMRA-UNIVERSITE—6, Boulevard du Maréchal Juin—14050 Caen Cedex, France

In situ FTIR spectroscopy has been used to investigate the adsorption of acetonitrile at room temperature onto zirconia activated at various temperatures (423, 723 and 873 K), attention being focussed on the sample pretreated at 423 K. Two acetamide monoanions (CH_3CONH^-), called α and β species, were spectroscopically evidenced with main bands, respectively, at 1169, 1432, 1590, 3320 cm^{-1} and at 1196, 1471, 1557, 3340 cm^{-1}. The use of ^{18}O- or D-labelled compounds gave poor results as far as the vibrational mode description was concerned, except for the $\delta(NH)$ mode. However, the H → D substitution was very useful for determining mechanisms. It was proposed that the β-type acetamide species results from H_2O displacement from the surface and CH_3CN adsorption in acidic Lewis sites, followed by a hydroxylation of this latter species by H_2O readsorption. The formation of the α-type acetamide species was thought to be due to a direct interaction of acetonitrile with basic OH groups. Upon heating at a temperature higher than 373 K and in the presence of water vapour, acetamide species were hydrolysed into acetate species.

Acetonitrile has been used as a spectroscopic probe to characterize the acidity and basicity of divided metal oxides. Owing to the nitrogen electron lone pair, it can be used as a base or electron donor. The $\nu(C{\equiv}N)$ wavenumber increases when electron donor–acceptor complexes $CH_3CN \cdots A$ are formed, A being a Lewis[1–3] or a Brønsted acid site.[4] With strong Brønsted acids, protonation occurs[5] giving rise to a high $\Delta\nu(C{\equiv}N)$ shift (*ca.* 75 cm^{-1}); however, this is still less important than that observed (*ca.* 110 cm^{-1}) when CH_3CN is complexed with carbocations.[6]

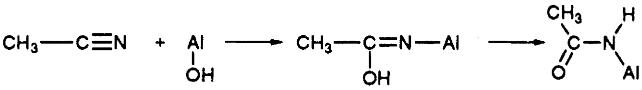
When the molecule is free, the $\nu(C{\equiv}N)$ vibration of CH_3CN is observed at 2251 cm^{-1} but is affected by a Fermi resonance with the $\nu(C{-}C) + \delta(CH_3)$ combination, then lying at 2287 cm^{-1}.[7,8] This Fermi resonance perturbs the determination of the $\nu(C{\equiv}N)$ shift in complexes.[9] Therefore use of CD_3CN is preferred for surface acidity measurements[10–12] since in this molecule, the $\nu(C{\equiv}N)$ vibration, observed at 2265 cm^{-1}, is not perturbed, even if it is difficult to exclude completely couplings with $\nu(CD_3)$ vibrations. However, CD_3CN adsorption on incompletely dehydroxylated metal oxides can lead to H → D exchanges with surface hydroxy groups, as reported for instance in the case of δ-alumina,[13] with a concomitant formation of partially deuteriated or even undeuteriated acetonitrile.

Hydrogen atoms of CH groups α to the $C{\equiv}N$ bond, such as those of the methyl group of acetonitrile, present a proton donor character, in such a way that the formation of the CH_2CN^- carbanion can be observed from the rupture of a C—H bond. When the cation is Na^+ or Li^+, the $\nu(C{\equiv}N)$ of the carbanion has been reported near 2050 cm^{-1}.[14] On a metal oxide, the following reaction occurs:

$$O^{2-}(surf) + CH_3CN \rightarrow OH^-(surf) + CH_2CN^-(ads)$$

The reaction involves the acid–base character of the OH^-/O^{2-} and CH_3CN/CH_2CN^- couples; moreover, it requires the participation of a cationic adsorption site to stabilize the CH_2CN^- carbanion. The $\nu(C{\equiv}N)$ of the carbanion characterizes the cationic site: as an example, it is observed at 2098 cm^{-1} in the case of unreduced ceria (adsorption site: Ce^{4+}) but it is at 2026 cm^{-1} after surface reduction (adsorption site: Ce^{3+}).[15] Polymerisation can occur leading in particular to the formation of the acetonitrile dimer monoanion,[15,16] and complicating the spectrum analysis.

Therefore, owing to its basic and acidic character, acetonitrile appears to be a very sensitive probe for determining the surface properties of metal oxides. However, it can also react with surface hydroxy groups, as has been shown in homogeneous catalysis;[17] acetic acid and ammonia are then formed. The catalysis is either basic or acidic. The reaction process is first the hydration of acetonitrile to acetamide, then a rapid hydrolysis to acetic acid.[18] On the surface of metal oxides like alumina, the reaction can be limited to the formation of the acetamide species:[19]

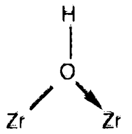


$$CH_3{-}C{\equiv}N + \underset{\displaystyle OH}{Al} \longrightarrow CH_3{-}\underset{\displaystyle OH}{C}{=}N{-}Al \longrightarrow \underset{\displaystyle O}{\overset{\displaystyle CH_3}{C}}{-}\underset{\displaystyle Al}{\overset{\displaystyle H}{N}}$$

Such a reaction supposes a polarisation of the $C{\equiv}N$ bond by the Al^{3+} cation, before the nucleophilic attack of OH^- groups. An analogy with the interaction between basic OH groups and CO_2 leading to the formation of hydrogen carbonate species can be considered. However, the hydrogen carbonate adsorption on the surface does not occur at the C—O(H) group level, which makes it difficult to generalize the CN(H) → Al adsorption structure represented in the scheme above. The presence of the acetamide monoanion species CH_3CONH^- has been considered in the case of ZnO,[20] Fe_2O_3[21] and MgO.[22] However, its spectroscopic characterization is still unclear, the spectral assignment being proposed from the qualitative comparison with spectra obtained from acetamide adsorption. When adsorbing CH_3CN on dehydroxylated ceria, the formation of the acetamide dianion CH_3CON^{2-} has been reported.[15] Benzonitrile adsorption on mixed oxides V-Sb-BiO supported on alumina led to the formation of $C_6H_5CONH^-$ and $C_6H_5CON^{2-}$ species.[23]

The aim of this work is to characterize the formation of CH_3CONH^- species when acetonitrile interacts with surface hydroxy groups of zirconia. ZrO_2 activated under vacuum at temperatures higher than 423 K presents two types of hydroxy groups, characterized by $\nu(OH)$ bands at 3775 and 3670 cm^{-1}, corresponding to monodentate (type I) and bidentate (type II) structures:[24,25]

(I)



(II)

In the bidentate structure, the free electron pairs of the oxygen atom are strongly engaged in the interaction with Zr^{4+} ions; only type I OH groups leads to the formation of hydrogencarbonate species in the presence of CO_2.[25] The isotope OH → OD exchange is quite easy with D_2O and $[^2H_6]$acetone.[24] Type I hydroxy groups are particularly reactive, being substituted by chloride ions when in contact with deuterochloroform, or giving rise to isopropylate groups in the presence of $[^2H_8]$propan-2-ol.[24] The specific reactivity of type I OH groups has also been shown through the formation of formate by adsorbing CO.[26] Zirconia shows interesting properties, such as alkene hydrogenation and isomerization.[27] Moreover, this metal oxide is often used as a support for metal catalysts with possible application in the treatment of post-combustion exhaust gases.

The aim of the present work is to study the reactivity of zirconia hydroxy groups by adsorbing acetonitrile at room temperature. Isotopic $^{16}O \rightarrow {}^{18}O$ and H → D substitutions have been used to characterize spectroscopically the acetamide species formed.

Experimental

ZrO_2 was prepared by hydrolysis of zirconium *n*-propylate in 70% propan-2-ol. The precipitate was filtered and washed five times with distilled water. The product was dried for 18 h at 393 K, then calcined under flowing oxygen (20 cm^3 min^{-1}) at 823 K. The zirconium oxide obtained had a mixture of tetragonal and monoclinic structures poorly crystallized and its specific area was 70 m^2 g^{-1}.

For IR studies, the samples were pressed into discs (10 mg cm^{-2}) and evacuated at 423 K. All the spectra were recorded at room temperature with a Nicolet MX-1 FTIR spectrometer.

Isotopic exchange (OH → OD) of the zirconia surface was realized by heating the sample at 423 K under D_2O vapour, the sample being previously evacuated at 423 K. The treatment was repeated three times. The same procedure was used to perform $^{16}O \rightarrow {}^{18}O$ isotopic exchange with $H_2{}^{18}O$.

Results

Characterization of Adsorbed Species

Acetonitrile was introduced by increasing doses on the activated sample. The spectrum obtained when the surface was approximately saturated by adsorbed species is shown in Fig. 1(*a*). Those resulting from the introduction of large amounts of CH_3CN ($P = 1.3$ kPa) followed by evacuation at room temperature are also reported in Fig. 1(*b*) and (*c*), respectively. Outgassing desorbs weakly adsorbed species. They result from the associative adsorption of CH_3CN and are mainly characterized by $\nu(C{\equiv}N)$ bands at 2252, 2283 and 2314 cm^{-1} and by a contribution to absorptions observed at 2985 and 2928 cm^{-1} [$\nu(CH_3)$ vibrations], 1440 and 1375 cm^{-1} [$\delta(CH_3)_{as}$ and $\delta(CH_3)_s$ vibrations, respectively], 1037 cm^{-1} [$\rho(CH_3)$] and 931 cm^{-1} [$\nu(C{-}C)$]. The 2283 cm^{-1} $\nu(C{\equiv}N)$ band and that at 2314 cm^{-1} (Fermi resonance) are mainly present in spectrum a of Fig. 1 and are due to CH_3CN adsorption on Lewis acid sites. The 2252 cm^{-1} band, strong in the presence of gaseous CH_3CN [Fig. 1(*b*)] is due to the formation of physisorbed species, the corresponding combination band contributing to that at 2283 cm^{-1}.

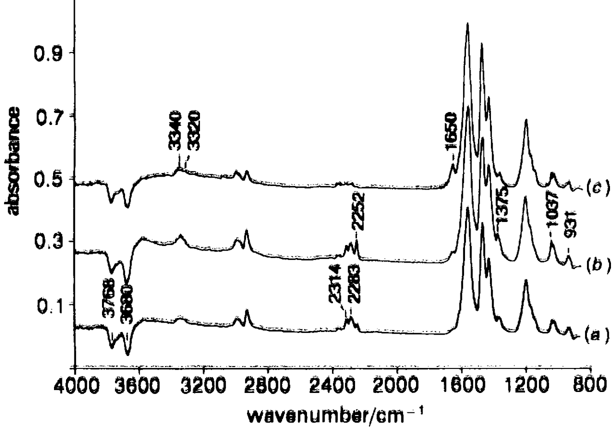


Fig. 1 Adsorption of CH_3CN on ZrO_2 activated at 423 K: (*a*) 540 μmol g^{-1}, (*b*) under 1.3 kPa of CH_3CN and (*c*) after evacuation

In the $\nu < 1650$ cm^{-1} frequency range, the main bands observed characterize the formation of acetamide species.[19] Their formation explains the decrease of the $\nu(OH)$ band intensity at both 3768 and 3680 cm^{-1}, as evidenced by the appearance of 'negative' absorbances in Fig. 1, which represents the difference of the absorbance of the sample before and after acetonitrile adsorption. The weak bands at 3340 and 3320 cm^{-1} are situated in the frequency range expected for the $\nu(NH)$ absorption of acetamide species. The $\nu(CH_3)_{as}$ and $\nu(CH_3)_s$ bands at 2985 and 2928 cm^{-1} decrease in intensity but partially remain after non-dissociated CH_3CN desorption [Fig. 1(*b*) and (*c*)] showing that they are due to both acetamide and undissociated CH_3CN species, the contribution of the latter to the $\nu(CH_3)_s$ band being predominant.

Several acetamide species are evidenced from either the adsorption of acetonitrile in different amounts, or acetonitrile adsorption on zirconia samples activated at different temperatures, *i.e.* weakly or highly dehydroxylated. As shown in Fig. 2, introduction of successive doses of CH_3CN gives rise to two sets of three bands, denoted [A, B, C], in the 1650–1100 cm^{-1} frequency range. They characterize two kinds of

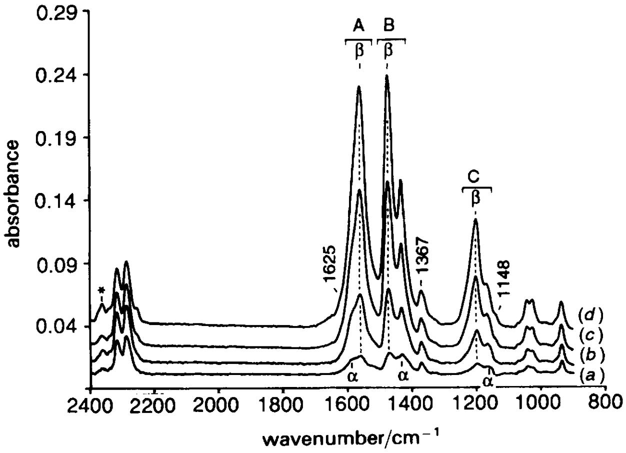


Fig. 2 Adsorption of CH_3CN on ZrO_2 activated at 423 K: (*a*) 45, (*b*) 90, (*c*) 135 and (*d*) 180 μmol g^{-1}. A, B and C correspond to bands relative to CH_3CONH^- α and β species. (see text). The asterisk marks CO_2 in the optical pathway.

acetamide species denoted α [1590 (A), 1432 (B) and 1169 (C) cm^{-1}], and β [1557 (A), 1471 (B) and 1196 (C) cm^{-1}]. When the introduced amount of acetonitrile is small [Fig. 2(*a*)], the intensities of the homologous bands due to α and β species are similar, but for higher coverage [Fig. 2(*d*)] bands due to β species predominate. The 1367 cm^{-1} band is essentially due to the $\delta(CH_3)_s$ vibration of undissociated CH_3CN. Note that other bands of A type (1625 cm^{-1}) and C type (1148 cm^{-1}) appear as shoulders when the amount of adsorbed species increases [Fig. 2(*d*)], but their intensity is too weak to be characterized accurately. Another absorption of A type is also noted at 1650 cm^{-1} when saturation is reached [Fig. 1(*c*) and (*d*)].

Fig. 3 presents spectra resulting from CH_3CN adsorption on ZrO_2 activated at increasing temperatures (423, 723 and 873 K), *i.e.* on an increasingly dehydroxylated sample. It appears that the formation of β-type acetamide species occurs when the activation temperature is low [Fig. 3(*a*)] whereas it is, relatively, not very important on the sample activated at 873 K [Fig. 3(*c*)]. By contrast, the formation of α-type acetamide species does not clearly appear to depend on the activation temperature. This behaviour allows one to assign the 3340 cm^{-1} ν(NH) band, whose intensity sharply decreases with the surface dehydroxylation, to β species. The shoulder at 3320 cm^{-1} and the broad absorption down to 2600 cm^{-1} can be assigned to the α species. In the spectrum relative to zirconia activated at 873 K [Fig. 3(*c*)], *i.e.* almost completely dehydroxylated, the formation of acetamide species [essentially of α type] does not imply the consumption of hydroxy groups, as shown by the comparison of the 3800–3600 cm^{-1} frequency range before and after CH_3CN introduction. Therefore any direct quantitative correlation between the decrease of the ν(OH) bands' intensity and the increase of A, B, C bands due to acetamide species is experimentally excluded; this is certainly due to the great disparity between the molar absorption coefficients of ν(OH) bands on one hand, and that characterizing acetamide species, on the other hand. Therefore, the formation of acetamide species from the interaction with residual water traces in the IR cell resulting from the *in situ* dehydroxylation of the sample cannot be excluded. The decrease of the amount of β species formed when the activation temperature increases, is accompanied by a stabilization of coordinated CH_3CN species, as shown from the study of the 2313 and 2290 cm^{-1} band intensities [Fig. 3(*b*) and (*c*)]. Moreover, the intensity of these bands seems to decrease slightly whereas that of the bands at 2125 and 2155 cm^{-1} increases [Fig. 3(*b*) and (*c*)]. The 2125 cm^{-1} band characterizes the formation of the acetonitrile CH_2CN^- monoanion, that at 2155 cm^{-1} results from its polymerization.[15] When CD_3CN is used, the two bands are observed at 2113 and 2160 cm^{-1}.

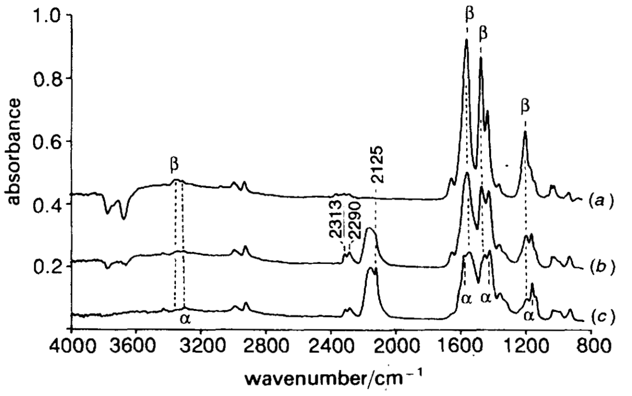


Fig. 3 Adsorption of CH_3CN (1.3 kPa then evacuation) on ZrO_2 activated at (*a*) 423, (*b*) 723 and (*c*) 873 K

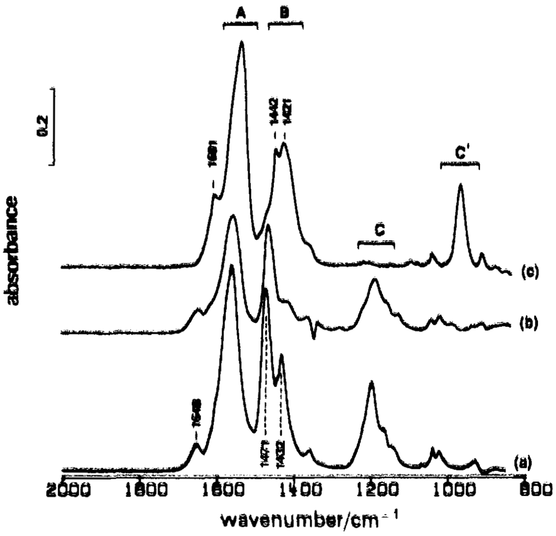


Fig. 4 Adsorption (1.3 kPa) then evacuation of acetonitrile on zirconia activated at 423 K: (*a*) CH_3CN on zirconia $ZrO_2(OH)$, (*b*) CH_3CN on zirconia exchanged by $H_2{}^{18}O$ and (*c*) CD_3CN on zirconia exchanged by D_2O,ZrO_2 (OD).

Characteristic Vibrations of α- and β-Type Acetamide Species

Adsorption has been performed on zirconia activated at 423 K. In addition to CH_3CN adsorption on ZrO_2 (^{16}OH), CH_3CN has been adsorbed on ZrO_2 (^{18}OH), whose hydroxy groups have been pre-exchanged by $H_2^{18}O$, and CD_3CN on $ZrO_2(^{16}OD)$, whose hydroxy groups have been pre-exchanged by D_2O. Spectra obtained after saturation by acetonitrile and then evacuation at room temperature are shown in Fig. 4. In such conditions, bands due to β species predominate, rendering the characterization of α species difficult.

Proposing the CH_3CONH^- structure for the acetamide species, the wavenumbers of characteristic bands for all the isotopic substitutions used are gathered in Table 1. The A band of the α species is generally not resolved and only an approximate wavenumber can be determined. For CD_3COND^-, the assignment of B bands at 1442 and 1421 cm^{-1} is ambiguous. We assign them to α and β species, respectively, according to their relative broadness; since in the case of CH_3CONH^- [Fig. 4(*a*)], the B band at 1432 cm^{-1} corresponding to α species is sharper and weaker than that at 1471 cm^{-1} due to β species, we assign, using the same criterion, the 1442 cm^{-1} band to α species and that at 1421 cm^{-1} to β species in the case of CD_3COND^- [Fig. 4(*c*)].

Reactivity of Adsorbed Species

Zirconia activated at 423 K essentially presents two ν(OH) bands at 3770 cm^{-1} (type I OH), and at 3675 cm^{-1} (type II OH), the intensity of the latter being stronger [Fig. 5(*a*)].

Table 1 Wavenumber (in cm^{-1}) of characteristic vibrations of α- and β-type CH_3CONH^- species adsorbed on zirconia

notation of bands	$CH_3C^{16}ONH^-$		$CD_3C^{16}OND^-$		$CH_3C^{18}ONH^-$	
	α	β	α	β	α	β
ν(NH), (ND)	3320	3340	—	2464	—	3340
A	1590	1557	(1560)	1530	—	1554
B	1432	1471	1442	1421	1419	1461
C	1169	1196	—	—	1157	1188
C′	—	—	962		—	—

Parentheses indicate that the band was difficult to detect.

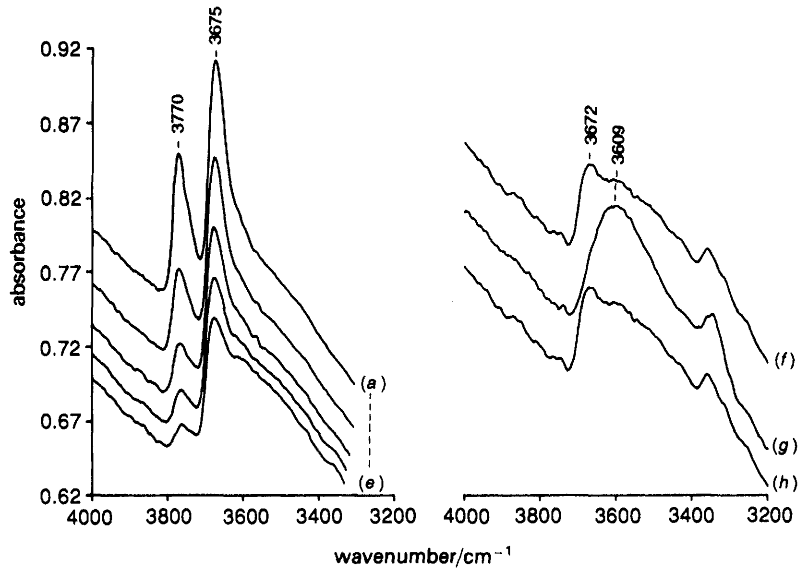


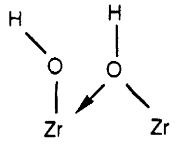
Fig. 5 ν(OH) vibrations of ZrO_2 activated at 423 K (*a*) and after adsorption of CH_3CN: successively 45, 90, 135, 180, 540 µmol g^{-1} (*b*)–(*f*); (*g*) under 1.3 kPa and (*h*) after evacuation.

Acetonitrile introduction by successive doses decreases their intensity by a similar amount [Fig. 5(*b*)–(*e*)]. Postulating that the molar absorption coefficient of the two ν(OH) bands is not very different, and that type I OH groups (OH^-) are more basic than type II ($O^{2-}H^+$), it is possible to deduce the following reaction balance:

$$OH^-(I) + O^{2-}H^+(II) \rightarrow O^{2-}(surf) + H_2O(gas) + \square$$

in which □ is an anionic vacancy.

Such a reaction is limited by the number of type I OH, initially less than that of type II. A version of Fig. 5 more detailed than that shown, would show that the 3675 cm^{-1} band (type II OH) has two components at 3682 and 3668 cm^{-1}. Dehydration essentially provokes the disappearance of the component at high wavenumber as noted in other work[28,29] in which the 3682 cm^{-1} band is assigned to an interaction between type I OH groups and coordinated water. In such a case, a shift from 3770 to 3682 cm^{-1} due to hydrogen bonding ($OH \cdots OH_2$) must lead to a broadening of the 3682 cm^{-1} band, whereas it appears sharp enough to be distinguished from the other component at 3668 cm^{-1}. We suggest that the distinction between the two components at 3682 and 3668 cm^{-1} is due to a difference in the neighbouring environment of the type II cationic adsorption sites. We propose that the 3682 cm^{-1} band, essentially affected by dehydration, is due to type II OH vibrations in the neighbourhood of type I ones:



When a large amount of CH_3CN is introduced (P = 1.3 kPa), the band due to residual hydroxy groups at 3672 cm^{-1} is shifted down to 3609 cm^{-1}, although it is broader and its intensity is stronger [Fig. 5(*g*)]. Outgassing [Fig. 5(*h*)] leads to repetition of the original spectrum [Fig. 5(*f*)]. This behaviour is typical of the formation of hydrogen-bonded species

$$OH(II) + CH_3CN_g \rightarrow OH \cdots N{\equiv}C{-}CH_3$$

The $\Delta\nu$ shift of the ν(OH) band (63 cm^{-1}) is close to that observed (76 cm^{-1}) for the cyclohexanol ν(OH) band in an interaction with acetonitrile in CCl_4 solution.[30] This allows us to estimate the acidity of type II OH groups: it is close to that of a secondary alcohol. However, note that under the conditions of this determination, acetamide adsorbed species can induce modifications of zirconia acidity.

Acetonitrile reactivity is *a priori* due to the acidity of its methyl group or to the basicity of the nitrile group. It has been shown in particular that the deuterium atoms of the methyl group of [$^2H_6$]acetone and [$^2H_8$]propan-2-ol were easily exchanged with the hydrogen atom of the hydroxy groups of zirconia.[24] Fig. 6 shows spectra resulting from the adsorption of CD_3CN on ZrO_2(OH) [Fig. 6(*a*)] or ZrO_2(OD) [Fig. 6(*d*)], and those relative to the adsorption of CH_3CN on ZrO_2(OD) [Fig. 6(*b*)] or ZrO_2(OH) [Fig. 6(*c*)]. Comparison of Fig. 6(*c*) and (*d*) shows that the 3800–3000 cm^{-1} range of ν(OH) or ν(NH) vibrations is similar to that of ν(OD) vibrations (2900–2200 cm^{-1}). Moreover, NH acetamide species can be distinguished from ND acetamide species by considering the C band at 1196 cm^{-1} [Fig. 6(*c*)] and C′ band at 962 cm^{-1} [Fig. 6(*d*)]. It is possible to consider that the molar absorption coefficients of C and C′ bands as roughly equal if the amounts of acetamide species are estimated from

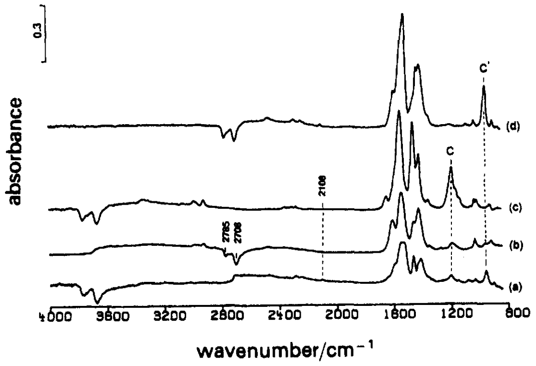


Fig. 6 Adsorption (1.3 kPa) then evacuation of acetonitrile on zirconia activated at 423 K: (*a*) CD_3CN on zirconia, ZrO_2(OH), (*b*) CH_3CN on zirconia exchanged by D_2O, ZrO_2(OD), (*c*) CH_3CN on zirconia, ZrO_2(OH) and (*d*) CD_3CN on zirconia exchanged by D_2O, ZrO_2(OD)

the intensity of bands in the 1600–1400 cm^{-1} range [Fig. 6(*c*) and (*d*)]. It is thus shown that the (—NH) and (—ND) acetamide species are formed in the ratio NH/ND = 1/2 in the case of CD_3CN adsorption on $ZrO_2(OH)$ [Fig. 6(*a*)] and in the ratio NH/ND = 2 in the case of CH_3CN adsorption on $ZrO_2(OD)$ [Fig. 6(*b*)]. Moreover, OH(I) and OH(II) groups [Fig. 6(*a*)] are affected according to the following features:

(1) total disappearance of type I hydroxy groups [absence of a ν(OD) band at 2785 cm^{-1}] and, as shown *vide infra*, of the equivalent amount of type II hydroxy groups (dehydration process);

(2) presence of type II OD groups, free (band at 2708 cm^{-1}) and associated (broad band below 2700 cm^{-1}).

The presence of type II free OH groups at 3676 cm^{-1} [Fig. 6(*c*)] can also be evidenced by the stronger decrease of the intensity of this band by isotopic exchange [Fig. 6(*a*)].

No $\nu(CH_3)$ band is observed near 2900 cm^{-1} after isotopic exchange OH → OD [Fig. 6(*a*)]; in contrast, the weak $\nu(CD_3)$ band is observed at 2108 cm^{-1} [Fig. 6(*a*)] with an intensity close to that observed at the same wavenumber in Fig. 6(*d*). It is concluded that in the adsorption of CD_3CN on $ZrO_2(OH)$, the deuteriation of hydroxy groups mainly occurs from gaseous CD_3CN. Taking into account the large amount of CD_3CN in the gas phase relative to the amount of OH groups of zirconia, acetonitrile remains mainly as CD_3CN. The H → D isotopic exchange of surface hydroxy groups is not correlated with the formation of acetamide species CD_3CONH^- and CD_3COND^- in a comparable amount. The lack of immediate correlation between the consumption of hydroxy groups and the amount of acetamide species formed also appears by comparison of Fig. 6(*a*) and (*c*): for a similar decrease of the intensity of ν(OH) bands near 3700 cm^{-1}, the intensities of acetamide bands in the 1600–1400 cm^{-1} range are quite different.

When CH_3CN is added by doses on $ZrO_2(OH)$, within an experimental time of *ca.* 15 min, spectra analogous to Fig. 1(*a*) are obtained. We can therefore measure, as a function of CH_3CN adsorbed, the amount of the following species: type I OH band at 3770 cm^{-1}, type II OH band at 3675 cm^{-1}, CH_3CN adsorbed on Lewis acid sites [combination band $\nu(C—C) + \delta(CH_3)$ at 2314 cm^{-1}], α-type acetamide species (B band at 1432 cm^{-1}) and β-type acetamide species (B band at 1471 cm^{-1}). The curves shown in Fig. 7 are then obtained. It appears that, for CH_3CN amounts lower than 135 μmol g^{-1}, the intensities of type I and type II ν(OH) bands decrease by the same amount [Fig. 7(*a*) and (*b*)]. For similar molar absorption coefficients, this leads to a ratio OH(I)/OH(II) = 1 for the hydroxy consumption which seems to be related to CH_3CN adsorption on Lewis acid sites [Fig. 7(*c*)]. When the amount of CH_3CN introduced is higher than 135 μmol g^{-1}, the intensity decrease of the band due to type II hydroxy groups is higher than that of type I, and then corresponds to a reversible physisorption of CH_3CN, evidenced by the ν(CN) band at 2255 cm^{-1} (not reported on Fig. 7). According to this result, zirconia dehydroxylation essentially appears as a dehydration reaction by CH_3CN adsorption on Lewis acid sites.

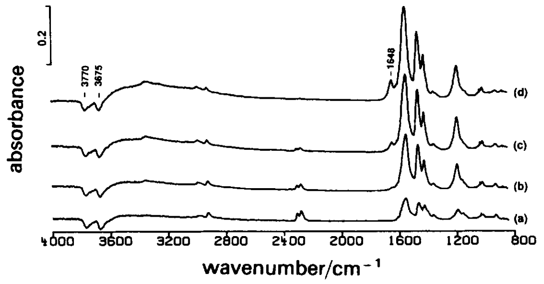


Fig. 8 Adsorption of CH_3CN (90 μmol g^{-1}) on ZrO_2 activated at 423 K. Time dependence: (*a*) 5 min, (*b*) 40 min, (*c*) 90 min and (*d*) 180 min.

Reactivity of CH_3CN *Adsorbed on Lewis Acid Sites*

Fig. 7 shows that, for an introduced amount of 200 μmol g^{-1}, the amount of CH_3CN on Lewis acid sites is a maximum [Fig. 7(*c*)] whereas Fig. 7(*d*) and (*e*) corresponding to acetamide species form an inflexion point. This indicates that the amount of adsorbed species depends not only on the amount of CH_3CN introduced, but also on time. CH_3CN chemisorbed on Lewis acid sites then appears as a reaction intermediate in the formation of acetamide species. In order to check the validity of this process, a small dose of CH_3CN (90 μmol g^{-1}) has been adsorbed on zirconia activated at 423 K, then the sample has been outgassed under a primary vacuum in such a way as to eliminate gaseous or physisorbed CH_3CN. The spectrum change is then followed with time (Fig. 8). It clearly appears on the figure that the intensity decrease of both ν(OH) bands at 3770 and 3675 cm^{-1} is similar and is effective as soon as CH_3CN is added. The variation of the relative number of species formed is shown in Fig. 9. The amount of α-type and β-type acetamide species is, as in Fig. 7, measured from the intensity of bands at 1432

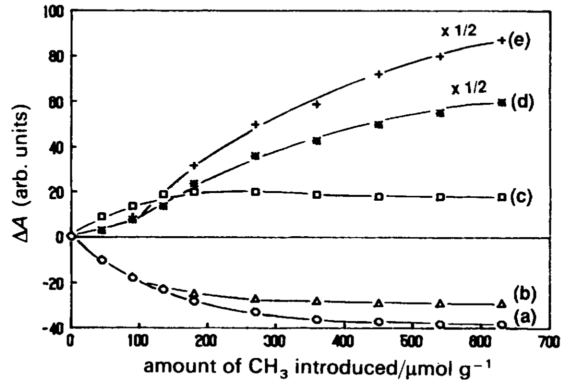


Fig. 7 Adsorption of CH_3CN doses (μmol g^{-1}) on ZrO_2 activated at 423 K. Relative variation of the quantity of adsorbed species: (*a*) hydroxy groups type II, OH(II), (*b*) hydroxy groups type I, OH(I), (*c*) coordinated CH_3CN on Lewis acid sites ($CH_3CN \rightarrow \square$ Zr), (*d*) α-type acetamide species, CH_3CONH^- and (*e*) β-type acetamide species, CH_3CONH^-. Variation in absorbance scale is marked by factors indicated on the curves.

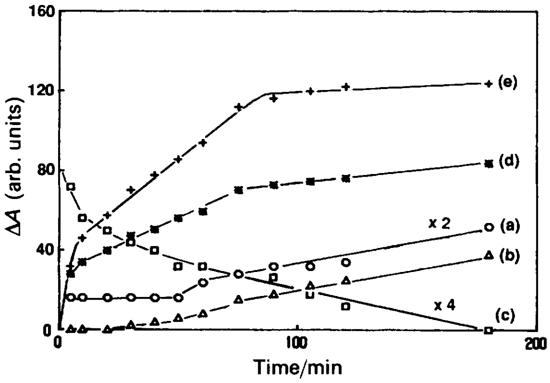


Fig. 9 Adsorption of CH_3CN (90 μmol g^{-1}) on ZrO_2 activated at 423 K. Evolution of absorbances: (*a*) at 3400 cm^{-1} and (*b*) at 1648 cm^{-1}. (*c*) Relative variation of coordinated CH_3CN species on Lewis acid sites, ($CH_3CN \rightarrow \square$ Zr), (*d*) α-acetamide species (CH_3CONH^-, α) and (*e*) β-acetamide species (CH_3CONH^-, β). Variation in absorbance scale is marked by a factor indicated on the curve.

[Fig. 9(*d*)] and 1471 cm^{-1} [Fig. 9(*e*)], respectively, whereas that of CH_3CN adsorbed on Lewis acid sites is measured from the intensity of the $\nu(C{\equiv}N)$ band at 2274 cm^{-1} [Fig. 9(*c*)]. The variation of the absorbance of a band at 3400 cm^{-1} [Fig. 9(*a*)] due to hydrogen bonded species and that of a well defined band at 1648 cm^{-1} [Fig. 9(*b*)] have also been reported.

Comparison of Fig. 9(*c*) with Fig. 9(*d*) and (*e*) shows that a good correlation occurs between consumption of CH_3CN adsorbed on Lewis acid sites and formation of α- and β-type acetamide species when $t < 90$ min. The comparison of the increase of the intensity sum of acetamide species B bands after 90 min of contact time and the corresponding decrease of the $\nu(C{\equiv}N)$ band intensity of species adsorbed on Lewis acid sites, indicates a ratio close to 12, which is effectively the order of the value of molar absorption coefficient, ε, ratios of the $\nu(C{\equiv}N)$ band of acetonitrile and the $\nu(C{=}O)$ bands of secondary amides, which can be roughly estimated from the study of compounds in the liquid phase: $\varepsilon = 15\ \text{l mol}^{-1}\ \text{cm}^{-1}$ for $\nu(C{\equiv}N)$ and $\varepsilon = 400\ \text{l mol}^{-1}\ \text{cm}^{-1}$ for $\nu(C{=}O)$.[31] As for hydroxy groups, ε can be considered close to $60\ \text{l mol}^{-1}\ \text{cm}^{-1}$ as observed for the $\nu(OH)$ of an alcohol,[31] *i.e.* a value close to that of $\nu(C{\equiv}N)$. Fig. 8(*a*) shows that the intensity of the $\nu(C{\equiv}N)$ band of acetonitrile coordinated to Lewis acid sites is of the same order of value than the intensity decrease of zirconia $\nu(OH)$ bands. All these results are compatible with a reaction process involving a fast zirconia dehydration step by acetonitrile adsorption on Lewis acid sites, followed by a slow reaction step of desorbed water with acetonitrile adsorbed on Lewis acid sites, leading to acetamide species.

Reactivity of Acetamide Monoanions

Comparison of Fig. 9(*b*) with Fig. 9(*d*) and (*e*) shows that the 1648 cm^{-1} [Fig. 9(*b*)] arises from the formation of a secondary species involving acetamide monoanions [Fig. 9(*d*) and (*e*)]. CD_3CN adsorption on $ZrO_2(OD)$ (Fig. 4) indicates that the 1648 cm^{-1} band is shifted to 1601 cm^{-1} when substituting H → D. It cannot be confused with the H_2O $\delta(HOH)$ vibration as its shift ($-47\ \text{cm}^{-1}$) is analogous to that observed for the A band of acetamide species (Table 1). The 1648 cm^{-1} band absorbance [Fig. 9(*b*)] increases like that of associated $\nu(OH)$ vibrations measured from the intensity of the 3400 cm^{-1} band [Fig. 9(*a*)]. This suggests that the 1648 cm^{-1} band results from solvation by water of acetamide monoanions, intermediate species in the acetamide hydration reaction to acetic acid.

Fig. 10 shows spectra (recorded at room temperature) obtained when acetonitrile has been adsorbed on zirconia activated at 423 K, the sample so obtained then being heated under vacuum at 323 and 373 K, or under a water atmosphere at 423 K. The latter treatment induces hydrolysis of acetamide species leading to the acetate ions characterized [Fig. 10(*c*)] by $\nu(OCO)_{as}$ and $\nu(OCO)_s$ bands at 1551 and 1450 cm^{-1}, $\delta(CH_3)$ at 1350 cm^{-1}, $\rho(CH_3)$ at 1021 cm^{-1} and $\nu(CC)$ at 943 cm^{-1}.[32]

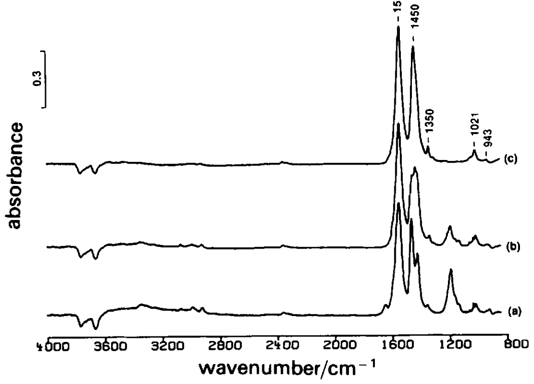


Fig. 10 Adsorption of CH_3CN on ZrO_2 activated at 423 K: IR spectra after heating under vacuum at (*a*) 323 and (*b*) 373 K, and after heating at 423 K in the presence of water vapour

The frequency difference between $\nu(OCO)_{as}$ and $\nu(OCO)_s$ bands is too small ($\Delta\nu = 100\ \text{cm}^{-1}$) to characterize a monodentate species (expected $\Delta\nu$ value: 250 cm^{-1}) and indicates either a bidentate ($\Delta\nu = 70\ \text{cm}^{-1}$) or a bridged ($\Delta\nu = 140\ \text{cm}^{-1}$) structure.[32] Acetate ion formation is hardly detectable after heating at 323 K [Fig. 10(*a*)], but is notable at 373 K [Fig. 10(*b*)].

The decrease of the number of acetamide species is evidenced by the concomitant decrease of the 1200 cm^{-1} band intensity. $\nu(OH)$ bands at 3768 and 3680 cm^{-1} do not seem affected; only associated $\nu(OH)$ and $\nu(NH)$ vibrations tend to disappear as acetate ions are formed. The intensity of bands in the 1600–1400 cm^{-1} frequency range (Fig. 10) does not change when acetamide species are transformed into acetate, which indicates that the molar absorption coefficients have similar values.

Discussion

α- and β-Type Acetamide Monoanion Vibrations

Vibrations of α- and β-type acetamide species, corresponding to bands A, B and C, can be described by comparison with spectra of CH_3CONH^- groups, as for instance in *N*-methylacetamide,[33] diacetylhydrazine anion $CH_3CONH{-}NCOCH_3^-$ [34] or CH_3CONH^- anion.[35] As in the *N*-methylacetamide spectrum, three bands analogous to those noted, namely amide I [80% $\nu(C{=}O)$ vibration, at 1653 cm^{-1}], amide II [$\delta(NH)$, $\nu(C{-}N)$ vibration, at 1567 cm^{-1}] and amide III [$\nu(C{-}N$, $\delta(NH)$, $\nu(C{-}C)$ vibration, at 1299 cm^{-1}][33] are observed.

The wavenumbers of the A, B and C bands (Table 1) are very close to those observed for acetamide monoanion with the following description:[34] $\nu(NCO)_{as}$ at 1559 cm^{-1}, $\nu(NCO)_s$ at 1419 cm^{-1} and $\delta(NH)$ at 1182 cm^{-1}. This confirms the acetamide monoanion nature of α- and β-type adsorbed species. Note that spectra of α and β species are notably oversimplified owing to the lack of bands specifically due to $\delta(CH_3)_{as}$ and $\delta(CH_3)_s$ vibrations. The weak band at 1365 cm^{-1} [Fig. 4(*a*)] survives after deuteriation [Fig. 4(*c*)] and appears only slightly perturbed after $^{16}O \rightarrow {}^{18}O$ exchange leading to a resonance splitting [Fig. 4(*b*)]. It cannot mainly be due to the $\delta(CH_3)_s$ vibration expected in this frequency range, but rather behaves as a B band of an acetamide-type adsorbed species.

From the isotopic shifts $^{16}O \rightarrow {}^{18}O$ and H → D (Table 1), it is possible to gain some information about the vibration descriptions. Note that the acetonitrile reactivity with zirconia did not allow one to obtain selectively CH_3COND^- and CD_3CONH^- species which then would permit us to distinguish between $CH_3 \rightarrow CD_3$ and NH → ND substitutions. In the case of the $^{16}O \rightarrow {}^{18}O$ substitution for the acetamide species which is better defined (β), the isotopic shift is notable only for B ($-10\ \text{cm}^{-1}$) and C bands ($-8\ \text{cm}^{-1}$) excluding a predominant $\nu(C{=}O)$ character for the A band. The H → D isotopic substitution shifts down the C-band wavenumber (*ca.* 1200 cm^{-1}) to about 240 cm^{-1} (C′ band at *ca.* 960 cm^{-1}). C and C′ bands are observed when CD_3CONH^- and CD_3COND^-, or CH_3CONH^- and CH_3COND^- are coadsorbed, indicating that C → C′ characterizes the NH → ND and not the $CH_3 \rightarrow CD_3$ substitution.

In the H → D isotopic substituion, the behaviour of the B band is very different depending on whether the α or β species are considered (Table 1). It decreases by 10 cm^{-1} in the case of the α species, and decreases by 50 cm^{-1} in that of the β species, indicating different intramolecular couplings which may be due to two different adsorption conformations.

Reaction Mechanisms

When acetonitrile interacts with zirconia dehydroxylated at 423 K, a fast step is observed including:

(i) the total disappearance of type I basic hydroxy groups (noted OH^-) through an acid–base dehydration reaction with type II acidic hydroxy groups (noted $O^{2-}H^+$);

(ii) hydrogen exchange of the residual type II hydroxy groups with the acetonitrile hydrogens as shown by CD_3CN adsorption;

(iii) an acetonitrile adsorption on Lewis-acid sites. This fast step is followed by a slower one involving the adsorbed acetonitrile hydroxylation into the CH_3CONH^- acetamide monoanion.

The slow step does not involve the participation of surface hydroxy groups; acetonitrile hydroxylation is thus limited by the re-adsorption by diffusion of water resulting from the fast dehydration step.

We therefore propose the following mechanism of the fast step:

$$OH^-(I)(surf) + CH_3CN(g) \rightarrow H_2O{,}CH_2CN^-(ads) \quad (1)$$

$$O^{2-}H^+(II)(surf) + H_2O{,}CH_2CN^-(ads) \rightarrow O^{2-}(surf) + \square + H_2O(g) + CH_3CN(g) \quad (2)$$

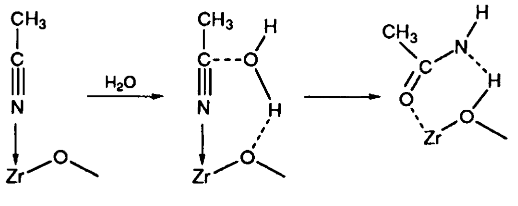
$$\square + O^{2-} + CH_3CN(g) \rightarrow CH_3CN(ads) + O^{2-} \quad (3)$$

Type II acidic hydroxy groups are able to exchange directly with $H_2O(g)$, as shown by the use of D_2O:

$$O^{2-}H^+(II)(surf) + D_2O(g) = O^{2-}D^+(II)(surf) + HDO(g) \quad (4)$$

In the first reaction, the basic character of type I hydroxy groups, adsorbed on Lewis acid Zr^{4+} cation sites [denoted □] is considered, as is the acid character of the hydrogens of the acetonitrile methyl groups. As in the case of the gas phase,[36] the CH_2CN^- monoanion solvation by H_2O is taken into account. Reaction (2) represents a proton transfer between the zirconia acidic hydroxy groups and the solvated acetonitrile monoanion, leading to the formation of a Lewis acid site Zr^{4+} by H_2O and CH_3CN desorption. Reaction (3) consists of CH_3CN adsorption on Lewis acid sites, the competitive water readsorption on such sites being neglected to take into account the large excess of CH_3CN in the gas phase.

The slow step is the hydroxylation reaction of CH_3CN adsorbed on Lewis acid sites. It is limited by H_2O (gas) diffusion:



(5)

The carbon attack by the hydroxy group of water is favoured by the electron donor character of the —C≡N group towards the Lewis acid sites Zr^{4+} (acidic catalysis). Water dissociation is favoured by the hydrogen bridge formation with the zirconia O^{2-} sites (basic catalysis). The intermediate structure of adsorbed H_2O was not spectroscopically detected because of either its short lifetime, or maybe its inactivity in absorption. The water molecule can be considered as adsorbed on the CH_3CN molecule, which presents a high longitudinal polarizability, in such a way that it is in a situation analogous to molecules adsorbed on metals. In the latter case, vibrations parallel to the surface are not spectroscopically active.[37] In the final geometry proposed for acetamide adsorption, the ν(NH) band is isolated (near 3300 cm^{-1}) only if there is no formation of an OH···NH hydrogen bridge. If a such formation occurs, the ν(OH) vibrations must, *a priori*, lead to a broad band near 3300 cm^{-1}, then coupled to the ν(NH) vibration, making the absorption spectroscopically very broad.

It is difficult to account for CD_3CONH^- and CD_3COND^- species formation in the ratio NH/ND = 1/2 when CD_3CN is adsorbed on zirconia (OH). The sole direct interaction process between CD_3CN and the hydroxy groups (then OD) giving selectively the CD_3COND^- species can be ruled out because deuteriation of surface hydroxy groups is very rapid compared with the rate of acetonitrile hydroxylation. In the mechanism proposed above, the NH/ND ratio depends on the isotopic composition of the water formed in the following reaction:

$$OH^- + CD_3CN \rightarrow HDO{,}CD_2CN^-(ads)$$

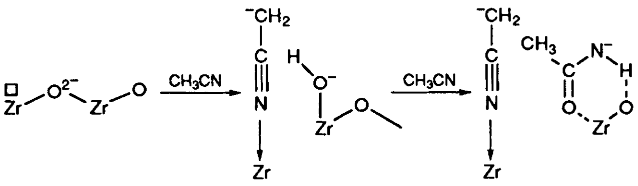
with OH/OD = 1 for water except if a statistical equilibrium is established in the $HDO{,}CD_2CN^-$ complex in which case OH/OD = 1/3.

The observed intermediate value of 1/2 for the NH/ND ratio may be due to isotopic exchange in reaction (4). However, this is also compatible with two different processes forming α- and β-type acetamide species. With this latter assumption, β species (essentially observed on hydroxylated surfaces) would be formed according to the above mechanism with NH/ND = 1, whereas α species (also observed on initially very dehydroxylated surfaces) would form by direct CD_3CN-hydroxy(OD) interaction, with NH/ND = 0. To retain two different mechanisms for α and β-type acetamide formation, we must account for experimental results which have shown that:

(i) the rates of formation of α and β species on a hydroxylated surface are related (Fig. 9).

(ii) the quantity of α species is nearly independent of surface dehydroxylation (Fig. 3). These species are even observed on a very dehydroxylated surface at 873 K.

To account for the latter result, we assume the presence of surface $Zr^{4+}O^{2-}$ pairs (weak acid–strong base) which, for a dehydroxylated surface, are liable to dissociate the weak acid CH_3CN to form the anions CH_2CN^- (ads) and OH^-. On a slightly dehydroxylated surface (activation at 423 K) no formation of CH_2CN^- is observed. Basic OH^- functional groups replace the basic O^{2-} considered above. The OH^- groups formed interact directly with CH_3CN (gaseous, physisorbed or adsorbed on Lewis acid sites) to form α-type acetamide species, according to the following idealized scheme (for a very dehydroxylated surface):



Apart from the intrinsic basicity of the OH^- groups, basicity of these hydroxy groups is likely to be induced by CH_2CN^- or CH_3CONH^- anions in the case of a hydroxylated surface. Note that the proton donor character of the α-type acetamide NH should lead to a broad ν(NH) band, whereas for β-type acetamide, the NH group is a proton acceptor. Hence the ν(NH) vibration of β-type acetamide is easier to spot (Fig. 3). It is difficult to justify the similar formation rates of α and β species, unequivocally. If the surface reaction is limiting, these can be determined by a common intermediate (CH_3CN adsorbed on Lewis acid sites). The reactions of α and β species formation could just as well be limited by diffusion of the gas mixture (H_2O–CH_3CN) in the intergranular space of the sample disc.

We can consider the following model of zirconia dehydroxylation by dehydration. Hydroxylated zirconia essentially comprises basic type I OH^- groups and acid $O^{2-}H^+$ type II groups. The basic OH^- groups are characterized by a ν(OH) of high wavenumber (3770 cm^{-1}), the acid hydroxy groups by a ν(OH) at 3661 cm^{-1}. The oxygen of the acid hydroxy groups belongs to the solid frame and is difficult to extract *a priori* in a non-reductive dehydroxylation. We therefore consider the dehydration to occur between the type I hydroxy groups and the hydrogen of type II OH. Two possibilities can be then envisaged according to the neighbourhood of Zr^{4+} sites made accessible by type I hydroxy elimination in the dehydration:

(i) if there were no type I hydroxy group in the immediate vicinity of a Zr^{4+} site, the latter would constitute a catalytic site (acid catalysis) for β-type acetamide formation by reaction with water.

(ii) if there was a type I hydroxy group in the immediate vicinity of Zr^{4+}, this hydroxy group becomes a type II with ν(OH) = 3682 cm^{-1}. This potentially basic hydroxy group is able to interact with acetonitrile to form the α-type acetamide species. It should not be confused with the lower wavenumber type II hydroxy (3661 cm^{-1}).

Our results of the study of acetonitrile adsorption to form the α- and β-type acetamide monoanions presents a strong analogy to those obtained in the study of hydrogencarbonate formation by CO_2 adsorption.[29] The formation of two types of hydrogencarbonates has been evidenced:

(i) one independent of the dehydroxylation state of the surface and formed with the OH corresponding to a wavenumber of 3682 cm^{-1} (analogously to α-type acetamide);

(ii) the other formed only on very hydroxylated surfaces [analogously to β-type acetamide] essentially from hydroxyls with ν(OH) 3775 cm^{-1}.

Conclusion

Two monoanions of adsorbed acetamide are spectroscopically evidenced by acetonitrile adsorption on zirconia. The first is denoted α and characterized by bands of acetamide type at 1590, 1432 and 1169 cm^{-1} and ν(NH) at 3320 cm^{-1}. The other, denoted β, is characterized by bands at 1557, 1471 and 1196 cm^{-1} with ν(NH) at 3340 cm^{-1}. Use of $^{16}O \rightarrow {}^{18}O$ and H → D isotopic substitutions shows that the corresponding vibrators are not intramolecularly localized apart from the band at lowest wavenumber (1169–1196 cm^{-1}) which is essentially a δ(NH) vibration.

Formation of the β structure of the acetamide monoanion, essentially on slightly dehydroxylated zirconia, has been interpreted by a water displacement reaction by acetonitrile with acetonitrile adsorption on Lewis acid sites followed by water interaction on this adsorbed form of acetonitrile. Formation of the α structure of the acetamide monoanion appears to be independent of the degree of zirconia hydration from direct interaction of specific pseudo-type II hydroxy groups with acetonitrile. These hydroxy groups are equivalent to type I (basic) hydroxy groups coordinated with Zr^{4+}. Adsorption of CH_3CN on the Zr^{4+} sites regenerates the type I structure. In the case of a very dehydroxylated surface, this type of hydroxy group should be obtained by dissociative adsorption of CH_3CN to form CH_2CN^-.

Hydrolysis of the acetamide species leads to acetate ion formation.

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