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FT-IR characterization of carbenium ions, intermediates in hydrocarbon reactions on H-ZSM-5 zeolites

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A series of N-alkylacetonitrilium ions were characterized by IR spectroscopy on an activated H-ZSM-5 sample pretreated by CD_3CN with various adsorbed olefins. Two kinds of $\nu(C\equiv N)$ band were evidenced according to whether the carbenium ion is secondary (2387 cm^{-1}) or tertiary (2376 cm^{-1}). The method is able to detect the isomerization intermediates of cyclohexene into methyl-cyclopentene.

Keywords: N-alkylacetonitrilium ions; secondary and tertiary carbenium ions; IR spectroscopy; olefin adsorption; deuterated acetonitrile; H-ZSM-5

1. Introduction

In a recent paper, Medin et al. [1] reported that CD_3CN adsorption on a H-ZSM-5 zeolite containing a small amount of propene pre-chemisorbed at 300 K led to the appearance of a strong band at 2370 cm^{-1}. They assigned it to the $\nu(C\equiv N)$ vibration of CD_3CN coordinated on a trigonal Al atom resulting from fission of the $Al \leftarrow O$ bond in bridged alkoxyl groups. Bystrov [2] explained it invoking the formation of nitrilium cations $[R'CNR]^+$ in which the R′CN base is complexed to the carbenium ion R^+, the latter acting as a very strong Lewis acid. This assignment was confirmed by use of deuterated propene: the 4 cm^{-1} shift observed clearly evidences that the nitrile CN group is really bound to the R^+ but not to the Al^{3+} ion of the zeolite framework [3]. It was concluded that nitriles can be used as a probe for the surface carbocation species which are important intermediates in hydrocarbon reactions catalysed by solids.

The aim of the present study is to extend the work to various alkenes in order to characterize tertiary, secondary and possibly primary carbenium ions, taking into account the fact that Olah and Kiovsky [4] showed that the $\nu(C\equiv N)$ frequency of N-alkylacetonitrilium tetrafluoroborates varied according to the nature

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of the alkyl group: CH_3 ($\nu = 2420\ cm^{-1}$), CH_3CH_2 ($2400\ cm^{-1}$) and $(CH_3)_3C$ ($2370\ cm^{-1}$).

2. Experimental

The zeolite used was a H-ZSM-5 sample with $Si/Al^{IV} = 29$. It was pressed into self-supported disks and activated by outgassing at 673 K. All the spectra, recorded with a Nicolet MAGNA 750 spectrometer, were registered at room temperature (r.t.).

Two procedures were used. The first (denoted A) is similar to that described in ref. [1] i.e. the olefin was first chemisorbed at r.t. and then CD_3CN was introduced. In the second (denoted B) the H-ZSM-5 sample was first saturated by CD_3CN and then evacuated at 423 K in order to regenerate about 10–20% of the initial Brønsted acid sites; finally, the olefin was introduced at r.t. (about 1 mole of olefin per mole of Brønsted acid sites).

3. Results

Since more information was gained using procedure B than procedure A, the results obtained first adsorbing CD_3CN, then the olefin, are discussed more fully.

The IR spectrum (fig. 1 (a)) of the activated zeolite shows two ν(OH) bands in the 3800–3600 cm^{-1} frequency range; the 3745 cm^{-1} band corresponds to silanol groups, that at 3612 cm^{-1} to the acidic framework SiOHAl groups. After chemisorption of CD_3CN (fig. 1 (b)), the silanol ν(OH) band is unaffected whereas the intensity of the framework hydroxyl band is about 20% that of the activated sample. The interaction between the perturbed SiOHAl groups and CD_3CN gives rise

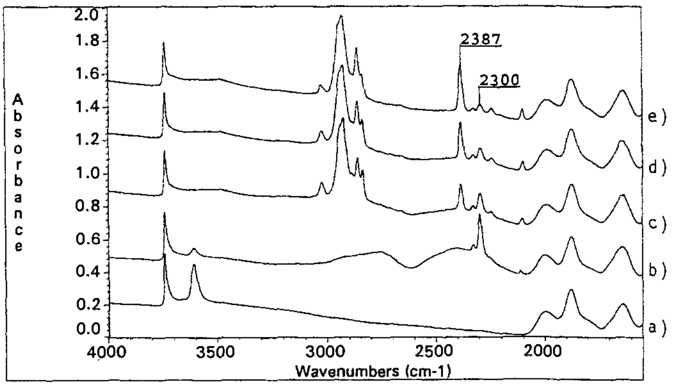


Fig. 1. IR spectra of cyclohexene adsorbed on H-ZSM-5 zeolite (procedure B). (a) Freshly pretreated sample, (b) after adsorption and evacuation of CD_3CN, (c) immediately after adsorption of cyclohexene, (d) after 5 min and (e) after 1 h.

to a sharp and strong $\nu(C\equiv N)$ band at 2300 cm^{-1}, to two broad bands at 2800 and 2400 cm^{-1} characteristic of a strong hydrogen bond and to a $\nu(CD_3)$ band at 2114 cm^{-1}. A weak band is also observed at 2330 cm^{-1} and indicates that a few CD_3CN molecules are coordinated to Lewis acid sites [5].

3.1. CYCLOHEXENE AND 1-METHYL-1-CYCLOPENTENE

Introduction of cyclohexene (fig. 1 (c)) on the sample thus treated leads to the complete disappearance of the 3612 cm^{-1} band whereas many bands are observed in the 3100–2800 cm^{-1} frequency range due to cyclohexene chemisorbed species. The important point is the appearance of a band at 2387 cm^{-1} at the expense of those previously seen at 2800, 2400 and 2300 cm^{-1}. The intensity of the 2387 cm^{-1} band increases further with time under a cyclohexene gas atmosphere, up to 1 h of contact, whereas that at 2300 cm^{-1} decreases. By analogy with refs. [2,3] the 2387 cm^{-1} is assigned to the $\nu(C\equiv N)$ vibration of a nitrilium ion.

The same features are observed using 1-methyl-1-cyclopentene instead of cyclohexene (fig. 2 (c)). However the band characteristic of the nitrilium cation is now at 2376 cm^{-1} and its intensity is a maximum just after olefin introduction.

It is important to note that when using procedure A and cyclohexene as olefin, the $\nu(C\equiv N)$ band of the nitrilium ion first formed is at 2385 cm^{-1} (fig. 3). It shifts to 2382 cm^{-1} after 1 h at 323 K and to 2377 cm^{-1} after heating at 573 K for 5 min. In each case the band is relatively broad and can be considered as the envelope of two bands at 2387 and 2376 cm^{-1}, their relative intensity varying with time or temperature.

3.2. PROPENE AND ISOBUTENE

Introduction of CD_3CN first and then propene (procedure B) evidences the pres-

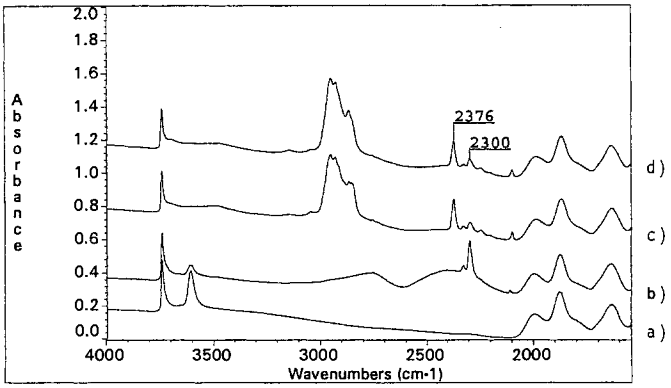


Fig. 2. IR spectra of 1-methyl-1-cyclopentene adsorbed on H-ZSM-5 zeolite (procedure B). (a) Freshly pretreated sample, (b) after adsorption and evacuation of CD_3CN, (c) immediately after adsorption of 1-methyl-1-cyclopentene and (d) after 1 h.

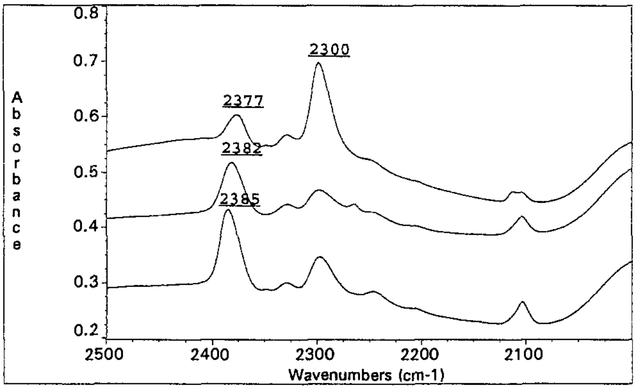


Fig. 3. Isomerization of cyclohexene adsorbed on H-ZSM-5 zeolite (procedure A). IR spectra recorded after: (a) 1 h at 298 K followed by adsorption of CD_3CN, (b) 1 h at 323 K followed by adsorption of CD_3CN and (c) 5 min at 573 K followed by adsorption of CD_3CN.

ence of two $\nu(C \equiv N)$ nitrilium ion bands at 2385 and 2373 cm^{-1} (fig. 4). Their intensity is initially similar but that at 2373 cm^{-1} becomes predominant with time. Note that use of procedure A leads to only one band at 2373 cm^{-1} in agreement with ref. [1].

Use of procedure B and isobutene as olefin also gives rise to a sharp band at 2377 cm^{-1}.

4. Discussion

Comparison of figs. 1 and 2 clearly shows that cyclohexene and its isomer

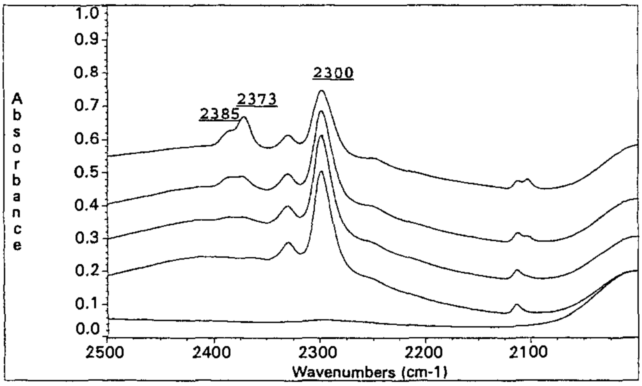
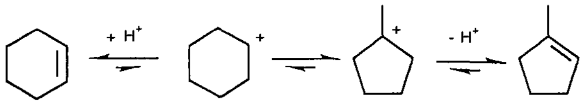


Fig. 4. IR spectra of propene adsorbed on H-ZSM-5 zeolite (procedure B). (a) Freshly pretreated sample, (b) after adsorption and evacuation of CD_3CN, (c) immediately after adsorption of propene, (d) after 5 min and (e) after 1 h.

1-methyl-1-cyclopentene do not lead to the same nitrilium cation, indicating that the complexed carbenium ion is itself different. Taking into account (i) the results of Olah and Kiovsky [4] indicating that the $\nu(C{\equiv}N)$ frequency in nitrilium complexes decreases when the substitution degree of the carbenium increases (tertiary < secondary < primary) and (ii) the highest stability of tertiary carbenium ions, we assign the 2387 cm^{-1} $\nu(C{\equiv}N)$ band to a nitrilium complex involving a secondary carbenium ion and that at 2376 cm^{-1} to a nitrilium complex involving a tertiary carbenium ion. A similar assignment is valid for propene, the nitrilium complex first formed involving a secondary carbenium ion which gives rise to a tertiary one with time (fig. 4). A tentative identification of the nitrilium complexes formed is given in table 1. It has not yet been possible to characterize the complexes involving primary carbenium ions.

The method permits detection of the two carbenium ions involved in the cyclohexene isomerization into 1-methyl-1-cyclopentene:



The higher stability of the 1-methyl-1-cyclopentyl cation causes the shift towards methyl-cyclopentene.

The present results therefore indicate that in previous experiments using procedure A [1,3] and propene as olefin, the carbenium ion complexed to CD_3CN was not the propyl cation but a tertiary cation certainly resulting from propene oligomerization. Use of a bulky olefin like cyclohexene reduces the transformation rate of the corresponding carbenium ion and allows its detection even using procedure A as shown in fig. 3. However, whatever the olefin, procedure B seems more appropriate for the characterization of the first carbenium ions formed. Examination of fig. 1 indicates the reason: on the Brønsted acid sites liberated by the partial elimination of CD_3CN, the olefin adsorption leads to the formation of a small number of carbenium ions. Their acidity being much higher than that of the activated zeolite, there is a displacement of CD_3CN bound to the surface towards the carbenium ions, creating the nitrilium ions and liberating Brønsted acid sites which can then protonate further molecules of olefin. This transfer of the probe molecule CD_3CN

Table 1
$\nu(C{\equiv}N)$ stretching frequencies in acetonitrilium complexes

Starting olefin	Ion $CD_3CN^+\underset{\mid}{\overset{\mid}{C}}H$ (cm^{-1})	Ion $CD_3CN^+\underset{\mid}{\overset{\mid}{C}}-$ (cm^{-1})
cyclohexene	2387	
1-methyl-1-cyclopentene		2376
propene	2385	2373 [a]
isobutene		2377

[a] Oligomers of propene.

from the SiOHAl groups towards carbenium ions well explains the variation with time of spectra reported in fig. 1 (c)–(e). After 1 h, we can expect that the number of nitrilium ions formed is close to that of Brønsted acid sites initially present.

Finally, the strength of the carbenium ions acidity, which is even higher when they are secondary as shown by the $\nu(C\equiv N)$ band, is quite remarkable. It is much higher than that of $AlCl_3$ ($\nu(CN) = 2330\ cm^{-1}$) or BF_3 ($2355\ cm^{-1}$) [6], whereas acidity of the H-ZSM-5, although generally considered high, is not sufficient for acetonitrile protonation (ν_{CN} expected at $2320\ cm^{-1}$ [5]). It is therefore concluded that under reaction conditions, the acidity of the system is not that of the starting zeolite but the acidity generated by the formation of carbenium ions. Note that it is the Brønsted acidity of the starting zeolite which is involved in the generation of carbenium ions whereas the formation of the latter creates strong Lewis acid sites. Therefore, there would be a change of the nature of acidic sites under reaction conditions. Further experiments are in progress to check this important point.

Acknowledgement

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