ELSEVIER

Catalysis Today 70 (2001) 227–241

CATALYSIS TODAY

www.elsevier.com/locate/cattod

# 2D-COS IR study of coking in xylene isomerisation on H-MFI zeolite[☆]

Frédéric Thibault-Starzyk*, Alexandre Vimont, Jean-Pierre Gilson

*Laboratoire Catalyse et Spectrochimie, ISMRA, 6 boulevard Maréchal Juin, F-14050 Caen Cedex, France*

## Abstract

*Ortho*-xylene isomerisation on H-MFI zeolite at temperatures between 393 and 573 K was studied in an infrared reactor-cell. 2D correlation analysis of the spectra recorded during the experiment allowed the detection of traces of coke on the catalyst, and the determination of the OH groups specifically perturbed by the coke molecules. Adsorption of collidine and pyridine on fresh and coked samples was used to determine the location of these OH groups in the microporous structure. It appears that coke is not perturbing Brønsted acidity (bridged OH) under these conditions on the MFI zeolite. It is mainly located on silanol groups; these silanols are not located on the external surface of the crystallites, but at defects located inside the pore system. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* H-MFI zeolite; 2D-COS IR study; Xylene isomerisation; Coke location; Collidine

## 1. Introduction

The results of IR experiments are almost displayed by plotting the absorbance (or transmittance) as a function of the frequency expressed in $\mathrm{cm}^{-1}$. This mode of representation is also called a 1D spectrum, and is encountered in other spectroscopies such as NMR where absorption is plotted as a function of the chemical shift expressed in ppm. NMR spectra, like IR ones, quickly become quite complex and useful information ever harder to extract. Complex NMR spectra can be presented in a more user-friendly manner by the so-called correlation spectroscopy (COSY) technique where different regions of the spectra are correlated. Such an approach and numerous related variants have enabled NMR spectroscopy to assert itself as a most powerful tool in the analysis of very complex dynamic phenomena [1]. A similar approach has not been used in the field of infrared (IR) spectroscopy, with the exception of the work of Noda et al. [2,3], working in the field of polymers. While it is obvious that such an approach could be applied to study chemical reactions occurring on the surface of heterogeneous catalysts, so far all IR studies in this domain are of 1D type. The 2D NMR approach is based on a double Fourier transform, the second being used to analyse the effect of a secondary magnetic pulse on the sample. This method strictly speaking cannot be applied to IR spectroscopy, but a transposition is possible if a periodic modulation is applied to the sample. The first Fourier transform is the usual one in FTIR, it extracts the IR spectrum from the interferogram. The second Fourier transform can then be used for a harmonic analysis which will indicate spectral correlations during the signal modulation. As stated above, this method has been introduced by Noda in the spectroscopy of an oscillatory strain of polymers, and is also applicable to non-periodically

---

[☆] Paper submitted for publication in a Special issue of Catalysis Today in honour of Jean Claude Lavalley.

* Corresponding author.

*E-mail address:* fts@ismra.fr (F. Thibault-Starzyk).

0920-5861/01/$ – see front matter
PII: S0920-5861(01)00420-5

varying systems, such as a chemical reaction on the surface of a heterogeneous catalyst.

IR spectroscopy is one of the major tools to study the surface of heterogeneous catalysts in working conditions [4–11]. This technique is referred to as "Dynamic in situ IR", as opposed to "Static in situ IR", where the catalyst is not under a continuous flow of reactants. Adsorbed species on the catalyst surface can then be monitored while at the same time the reaction products are analysed (GC, MS, etc.), under realistic catalytic conditions. Dynamic in situ IR contributed greatly to the determination of reaction mechanisms in the field of deNO$_x$ catalysis [11] or in hydrocarbon conversion and isomerisation reactions [4–8,10]. Interpretation of the spectra is not straightforward and is unfortunately quite often the limiting step of this technique for reasons such as:

- Surface species are numerous and their nature often unknown; adsorption modes can vary, and intermediates can be new and unexpected.
- The selection of the suitable bands for a quantitative monitoring of the relevant species can be very difficult.
- Detection of trace compounds is often a problem because of the low signal to noise ratio obtained at high temperature in the infrared cell.

We want to demonstrate that new data treatment methods such as 2D correlation IR spectroscopy (2D-COS) lead to significant improvements in this domain. We report the application of 2D-COS to the in situ infrared study of *ortho*-xylene isomerisation on a H-MFI zeolite catalyst in working conditions. This leads to improved quantitative monitoring of the xylene isomers in the zeolitic micropores and to the detection of traces of coke on the catalyst.

## 2. 2D correlation spectroscopy

2D-COS is a data treatment method leading to an easier analysis of complex infrared spectra. It was initially introduced by Noda et al. [2] for the interpretation of dynamic infrared dichroism spectra acquired under a sinusoidal perturbation, such as that produced by the mechanical strain of a vibrating polymer. Infrared absorption can vary with the constrain, because of reorientations of functional groups in the polymer. Infrared absorption varies with the dipolar moment of the vibrator, and with its orientation along the polarisation of the IR beam. This variation can happen in-phase with the deformation or with a phase shift. The polymer deformations being very limited, spectral variations are also very small, and not detectable on the direct spectra. The aim of Noda was, thus, to increase sensitivity for these weak variations. 2D-COS spectra are obtained by a Fourier analysis of the variation of the spectra with the perturbation:

$$\Phi(\nu_1, \nu_2) + \mathrm{i}\Psi(\nu_1, \nu_2) = \frac{1}{\pi T}\int_0^{\infty} Y_1(\omega) \cdot Y_2^*(\omega)\,\mathrm{d}\omega \tag{1}$$

where $Y_1$ and $Y_2^*$ are the Fourier transform and conjugated Fourier transform of the IR intensity variations during time $T$ at frequencies $\nu_1$ and $\nu_2$, respectively. $\omega$ is the Fourier frequency that corresponds to the frequency of the perturbation. Synchronous correlation is defined as $\Phi(\nu_1,\nu_2)$ and asynchronous correlation as $\Psi(\nu_1,\nu_2)$. Synchronous and asynchronous correlation indicate the level of correlation between changes in absorption bands in a spectral series (intensity, position, width) recorded during the perturbation. This analysis produces 3D graphs, with two axes for wavenumbers and one for intensity. In synchronous correlation graphs, autopeaks are observed on the diagonal for each varying band, and cross-peaks out of the diagonal indicate a correlation between bands at two separate wavenumbers, for which the changes are simultaneous. Asynchronous correlation gives information on non-correlated peaks; the graphs contain cross-peaks only, indicating IR bands for which the changes are not simultaneous. These bands are due to independent functional groups or to molecules in different environments. The main drawback of this method is that it could only be applied first to sinusoidal perturbations. Noda later generalised his method to non-sinusoidal perturbations such as irradiations or electrochemical perturbations [3], leading to significant increases in sensitivity and resolution of complex band groups. The synchronous spectrum can be calculated without the need of Fourier transform:

$$\Phi(\nu_1, \nu_2) = \frac{1}{T}\int_0^{T} y_1(\nu_1, t) \cdot y_2(\nu_2, t)\,\mathrm{d}t \tag{2}$$

where $y_1$ and $y_2$ are intensity variations at wavenumbers $\nu_1$ and $\nu_2$. Using a discrete sum in place of an integral, synchronous correlation corresponds to a statistical covariance analysis in the spectral series:

$$\mathrm{COV}(\nu_1,\nu_2)=\frac{1}{N}\sum_{i=1}^{i=N}((A_i(\nu_1)-\bar{A}(\nu_1)) \times (A_i(\nu_2)-\bar{A}(\nu_2))) \tag{3}$$

where $N$ is the total number of spectra recorded, $A_i(\nu_1)$ the absorbance at $\nu_1$ for the $i$th spectrum, $\overline{A}(\nu_1)$ the absorbance at $\nu_1$ for the reference spectrum. The reference spectrum is generally the arithmetic mean spectrum, but the first spectrum or the spectrum at steady-state can also be used. We will also use in this work $r(\nu_1,\nu_2)$, which is the statistical correlation coefficient between intensities at wavenumbers $\nu_1$ and $\nu_2$. This coefficient is traditionally used in 1D spectroscopy to measure the linearity of the correlation between two bands:

$$r(\nu_1,\nu_2)=\frac{\mathrm{COV}(\nu_1,\nu_2)}{\sigma_{\nu 1}\sigma_{\nu 2}} \tag{4}$$

where $\sigma_{\nu 1}$, $\sigma_{\nu 2}$ are the standard deviations at $\nu_1$ and $\nu_2$, respectively.

The asynchronous spectrum cannot be calculated rigorously without a Fourier transform, but a good approximation of its absolute value is obtained with the so-called disrelation spectrum:

$$\Lambda(\nu_1,\nu_2)=\sqrt{\Phi(\nu_1,\nu_1)\cdot\Phi(\nu_2,\nu_2)-\Phi^2(\nu_1,\nu_2)} \tag{5}$$

## 3. Experimental

Experiments are performed in a micro reactor-infrared cell already described elsewhere [4], in which the spectra of both the self-supported catalyst wafer and the adsorbed species are recorded during the reaction, up to a temperature of 725 K.

A nitrogen gas stream is diverted to a saturator filled with *ortho*-xylene, maintained at a constant temperature (300 K); the resulting mixture feeds the reactor/IR cell. The reaction conditions are: 473–573 K, 8 Torr *o*-xylene partial pressure, WHSV 2.7 $h^{-1}$. The reaction products exiting the reactor are analysed by gas chromatography. The IR spectrometer is a Nicolet Magna 750, with at 2 $cm^{-1}$ resolution (Happ-Genzel apodisation function) and fitted with a DTGS detector.

The MFI sample ($NH_4^+$ form) is commercially available from Conteka (CBV 5020 with a Si/Al = 29). Microporous volume and external surface area are 0.17 $cm^3\,g^{-1}$ and ca. 65 $m^2\,g^{-1}$, respectively (determined from a *t*-plot analysis of $N_2$ adsorption). Self-supported pressed discs (diameter 1.6 cm, 5–8 mg $cm^{-2}$) activated under a nitrogen flow (IR cell reactor) or under vacuum ($5 \times 10^{-6}$ Torr, IR quartz cell) up to 723 K (1 K $min^{-1}$), yield the dehydrated H-form of the zeolite.

In order to determine the various adsorption modes of 2,4,6-collidine, samples of silica (Grace Davison 432, surface area 310 $m^2\,g^{-1}$, pore volume 0.5 $cm^3\,g^{-1}$), Y-zeolite ($Si/Al_{TOT} = 5.5$, $Si/Al^{IV} = 5.4$, $a_0 = 24.47$ Å, obtained by ammonium hexafluorosilicate treatment of Zeocat E2268, initial Si/Al = 2.7) and a pure gamma alumina ($S_{BET} = 210\,m^2\,g^{-1}$, obtained by calcination (820 K, 1 h) of boehmite CONDEA Chemie, ref. SB3) are used. The samples are activated by slowly heating under vacuum (see text for activation conditions).

Probe molecules adsorption takes place in an IR quartz cell connected to a vacuum line. Collidine, pyridine and di-tertio-butyl pyridine (DTBP) from Aldrich (99+% grade) are dried on molecular sieves prior to their use.

## 4. Results and discussion

### 4.1. Interaction of xylenes with the catalyst at 473 K

The spectrum of the activated-MFI zeolite at 473 K (Fig. 1, inset) shows two intense bands at 3738 and 3602 $cm^{-1}$ in the $\nu$(OH) stretching vibration region. They are assigned to the stretching vibrations of (non-acidic) silanols and (acidic) bridged hydroxy groups, respectively. Upon *ortho*-xylene adsorption at this temperature (Fig. 1, inset), the intensities of both bands immediately decrease. Attenuation is moderate for the silanol band (10%), indicating only a weak interaction. The intensity decrease of the acidic hydroxy band is much more important (70% reduction) and can be assigned to the formation of a hydrogen bond with the aromatic ring. The perturbed OH group

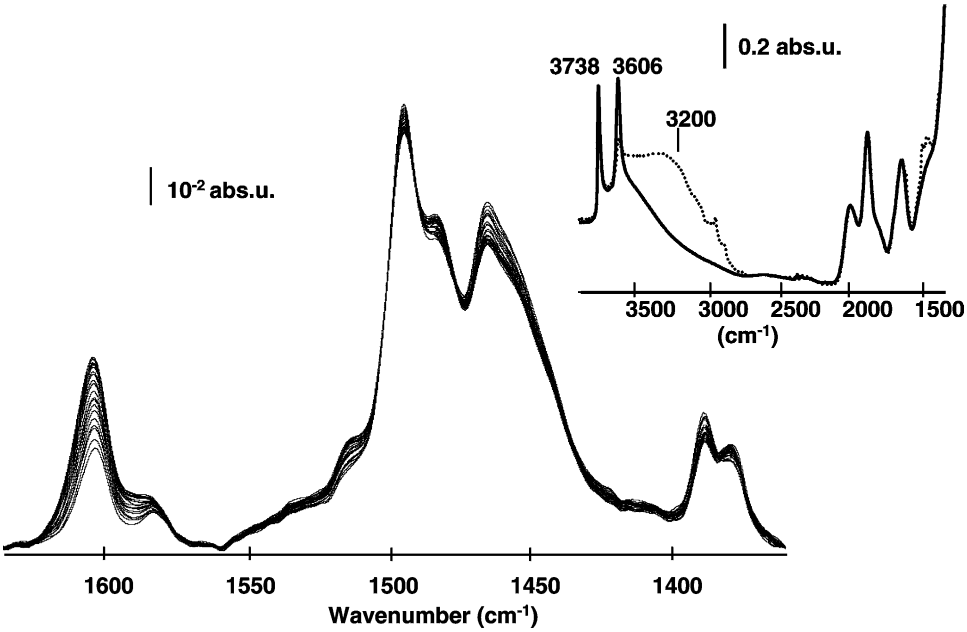

Fig. 1. Some of the spectra recorded between 4 and 14 min reaction time at 473 K. Inset: spectra of the clean catalyst (normal line) and of the same in working conditions (dotted line).

leads to a broad band centred around 3200 cm$^{-1}$. At the same time, a complex set of bands appears between 1380 and 1600 cm$^{-1}$ (Fig. 1) and is assigned to cycle vibrations of the adsorbed *ortho*-xylene. During the first minutes of reaction, a new band appears at 1605 cm$^{-1}$, assigned to $\nu_{8a}$ or $\nu_{8b}$ vibration of *meta*-xylene [12] (1610 cm$^{-1}$ in the liquid phase). Although *para*-xylene should exhibit an intense and characteristic band (1515 cm$^{-1}$ in the liquid phase [13]), it is not observed on the surface, but is present in the reaction products (GC analysis). This is most probably related to its fast diffusion in the pore system preventing its building up and detection inside the catalyst pores under our reaction conditions (2 ± 0.2% conversion).

The quantitative analysis of spectra for the measurement of the isomers concentration in the pore system is difficult, and is usually done by comparing the surface spectra with those of the pure isomers at room temperature. During the reaction, the spectra of the pure isomers are significantly altered, and anyway cannot be measured because of their fast isomerisation. Such a reactive system is, therefore, a good case to test the potential of the 2D-COS approach.

### *4.2. 2D-COS analysis of the IR spectra*

As already outlined above, the chemical reaction is considered as the perturbation in the 2D treatment in Eq. (1). In this particular case, we use the 2D-COS analysis of a series of spectra recorded between 4 and 14 min of reaction time in *o*-xylene isomerisation reaction to resolve the aromatic cycle vibration bands group (Fig. 1).

The synchronous correlation spectrum (Eq. (2)) is displayed in Fig. 2. In the following, we elect to split the synchronous correlation spectra in two separate sets for positive and negative values in order to identify bands correlated (positive synchronous correlation, Fig. 3) or anticorrelated (negative synchronous correlation, Fig. 4). During isomerisation, *ortho*-xylene is progressively replaced by *meta*-xylene which accumulates in the pore system. A negative correlation is, therefore, expected between the *ortho*-xylene (intensity decreases) and the *meta*-xylene bands (intensity increases). On the other hand, a band having contributions from *o*-xylene is correlated with other bands of *o*-xylene, while bands containing *m*-xylene contributions constitute a second group of peaks correlated

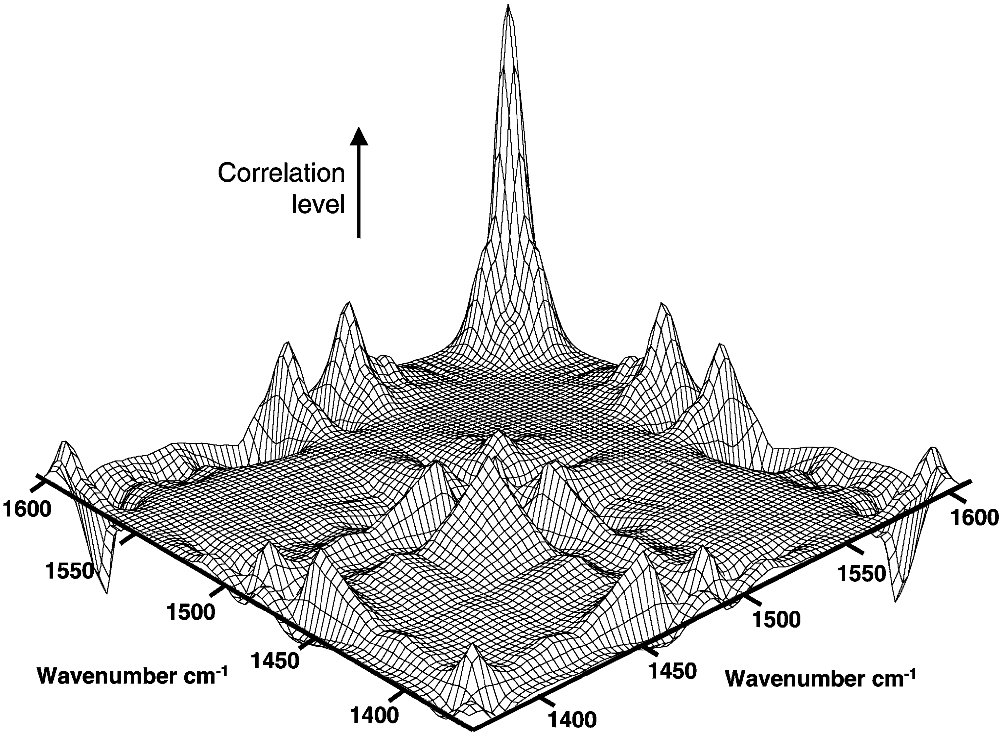

Fig. 2. Synchronous correlation spectrum obtained with 34 spectra recorded between 4 and 14 min reaction time at 473 K. On the diagonal band, autopeaks indicate the variance at each frequency in the 1D spectra; the most intense autopeaks indicate where the most important relative intensity changes take place in the spectra. Autopeaks are always positive. Out of the diagonal line are cross-peaks, indicating bands varying simultaneously in the spectra: positive cross-peaks for bands with intensities decreasing together or increasing together, negative cross-peaks for bands with intensities varying in opposite ways, one increasing while the second decreases, or one decreasing while the second increases. Positive cross-peaks, therefore, show the wavenumbers of two bands from the same chemical species, and negative cross-peaks indicate the wavenumbers of two bands from two separate species probably converted one into the other.

with each other. Assignment of bands is, thus, considerably eased. At 473 K, *m*-xylene bands (Fig. 5) are located at 1605, 1590, 1534, 1515, 1482 and 1381 $\text{cm}^{-1}$, while *o*-xylene bands are at 1495, 1466, 1458, 1423, 1412 and 1390 $\text{cm}^{-1}$. The spectral regions exhibiting the most intense negative covariance are chosen for the in situ quantitative monitoring: 1605 $\text{cm}^{-1}$ for *meta*-xylene, 1466 $\text{cm}^{-1}$ for *ortho*-xylene. The corresponding extinction coefficients for these two bands are determined by adsorbing the two pure isomers on the catalyst at 393 K (highest temperature achievable without isomerisation) under identical conditions in the infrared cell and in a thermogravimetric MacBain balance. The contribution of each isomer to both bands was measured. The values are, respectively, $\varepsilon_{1605}(\textit{meta}) = 0.026 \pm 0.004\,\text{cm}\,\mu\text{mol}^{-1}$ and $\varepsilon_{1466}(\textit{ortho}) = 0.029 \pm 0.004\,\text{cm}\,\mu\text{mol}^{-1}$. IR intensities (rather than area because of overlapping) of these two bands can then be used to measure the concentrations of the isomers in the pore system and their variation with time on stream (Fig. 6).

2D-COS is particularly powerful when applied to spectra recorded at high temperature, where the signal to noise ratio is low, such as during the reaction at 573 K. Correlation analysis with a great number of spectra favours the elimination of noise in infrared intensities and allows the detection of very weak bands, barely noticeable in the normal 1D spectra. After the initial adsorption step, the steady-state is reached but no change is visible in the 188 1D spectra recorded between the 5th and the 60th minutes time on stream (Fig. 7A); however, 2D-COS clearly

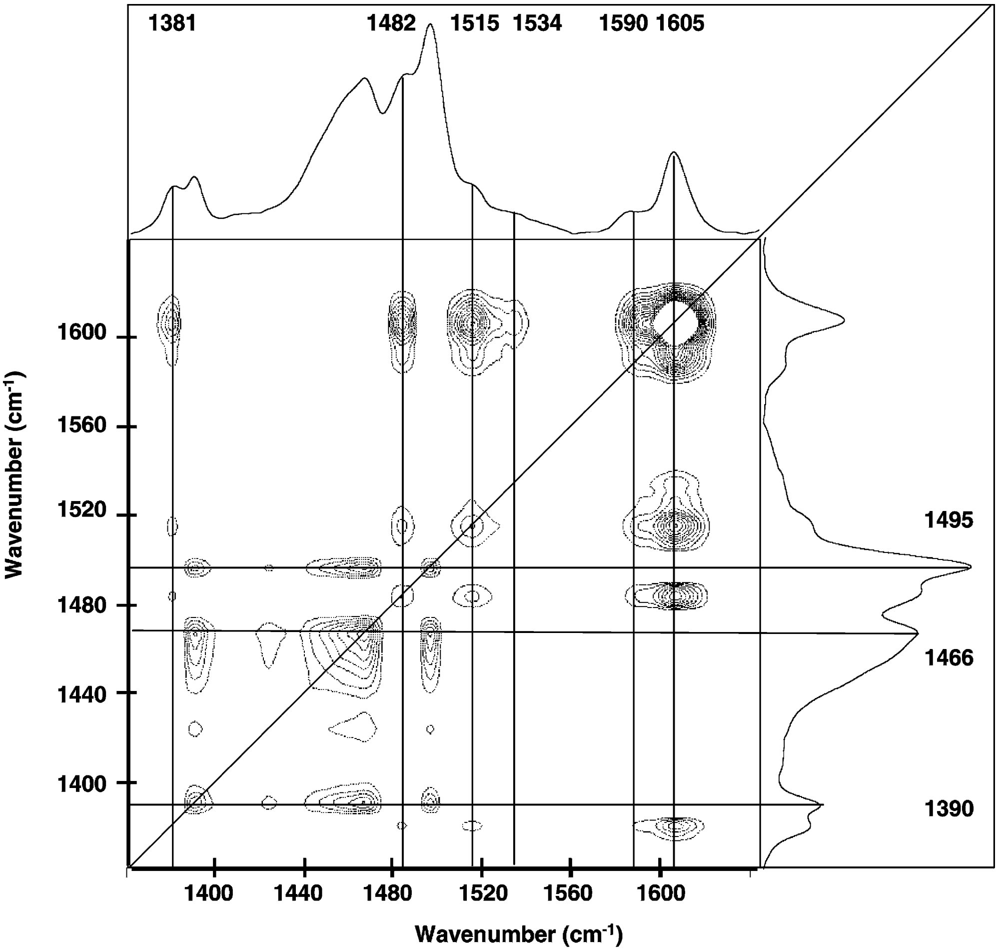

Fig. 3. Positive part of the 2D synchronous correlation map in Fig. 2. The spectra displayed on the axes are the mean spectra in the series, only showed to indicate where bands are located in the spectrum.

shows a cross-peak in the region of cycle vibrations at 1596 cm$^{-1}$ (Fig. 7B, right). Such a shoulder is not observed in the 1D direct spectra, because of overlapping by xylene bands at 1600 cm$^{-1}$; moreover, the background noise prevents the detection of any weak band in this region, even on difference spectra. It is, therefore, not possible to observe directly a correlation between this phenomenon and the variation in the $\nu$(OH) range with the usual 1D spectra. Again, the negative covariance map between the region of cycle vibrations and $\nu$(OH) bands (Fig. 7B, left) reveals a link between the emergence of the 1596 cm$^{-1}$ band and an intensity decrease of two specific bands located at 3727 and 3656 cm$^{-1}$. The linear decrease of these intensities and the emergence of the band at 1596 cm$^{-1}$ is estimated by the correlation coefficient $r$. The negative correlation map between these two spectral ranges is represented in Fig. 7C (left); it shows that a good linear correlation exists between the appearance of the band at 1596 cm$^{-1}$ and the consumption of the two hydroxy groups at 3656 and 3727 cm$^{-1}$ ($r < -0.8$).

By flushing the catalyst surface with pure helium at the reaction temperature, adsorbed xylenes are eliminated, and the corresponding bands disappear (Fig. 8). A species remains, however, adsorbed on the surface, and is characterised by a band at 1596 cm$^{-1}$. At the same time, bands corresponding to the $\nu$(OH) are not completely recovered, and (very) weak negative

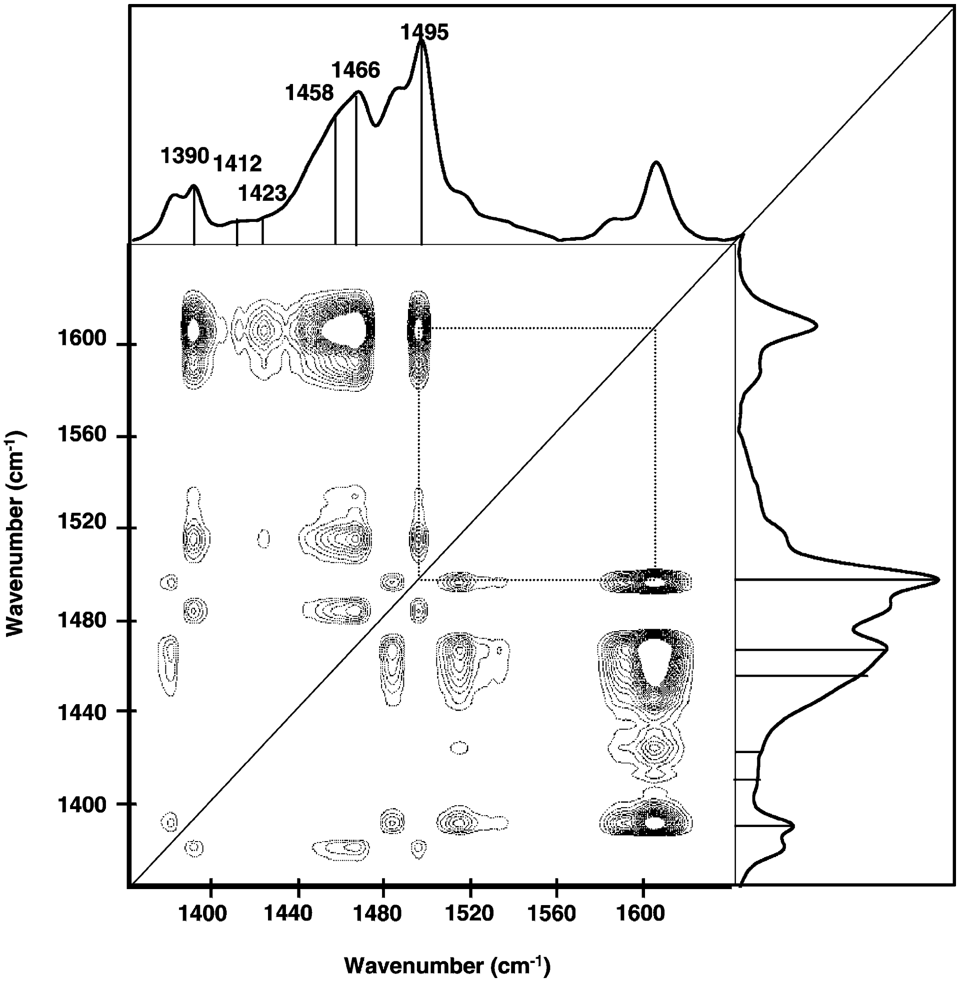

Fig. 4. Negative part of the 2D synchronous correlation map in Fig. 2. The spectra displayed on the axes are the mean spectra in the series, only showed to indicate where bands are located in the spectrum.

bands appear in the difference spectrum at 3727 and 3656 cm$^{-1}$. These observations confirm the 2D-COS results collected during the reaction: a slow and weak consumption of specific hydroxy groups by irreversibly adsorbed species formed in the course of the reaction. The evolution of the integrated intensity of the different IR bands as a function of time on stream (Fig. 9) illustrates this point. We interpret this result as traces of coke (bands around 1600 cm$^{-1}$ are generally observed after coke formation on zeolites in hydrocarbon conversion reactions [6–8,14]), located on these specific silanol and OH groups, but absent on the acidic (bridged OH) sites. Coke is only present in trace amounts, and catalytic activity remains constant (ca. 7%) throughout the reaction. In line with observation by others, a slight increase in *para*-selectivity is observed by GC analysis of the products.

### 4.3. Coke location

Species present on the catalyst surface during *o*-xylene isomerisation are detected by IR spectroscopy. Some specific OH groups are affected: the low frequency silanol groups are progressively perturbed

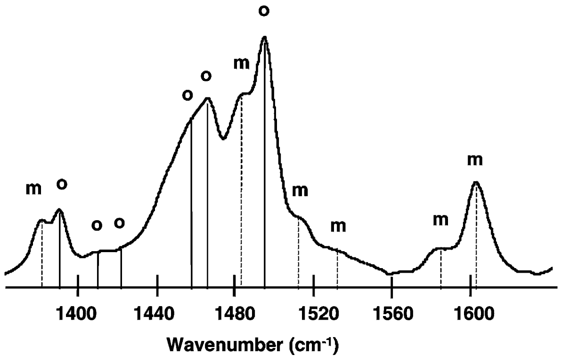

Fig. 5. Assignment of bands in the cycle vibration region to *o*- or *m*-xylene, based on 2D-COS analysis.

by coke deposition when the reaction is performed at 573 K. The exact location of these perturbed OH groups in the structure would greatly facilitate the location of coke in the pore system. The location of OH groups in MFI has already been studied by varying the size of probe molecules: acetonitrile–adamantane carbonitrile [15,16], acetonitrile–pivalonitrile [17]. The main conclusion was that a silanol band at 3730 cm$^{-1}$ is indicative of the presence of internal silanol group (located inside the micropores and not on the external surface of crystallites) [18]. The acidic bridged hydroxyls (band around 3610 cm$^{-1}$) are located inside the zeolite pores. We studied the adsorption of pyridine and 2,4,6-collidine (two basic probe molecules of different sizes) on a fresh and a used catalyst in static conditions, in an infrared quartz cell.

### *4.3.1. Adsorption of probe molecules on the fresh catalyst (Fig. 10)*

The room temperature spectrum of the activated catalyst (spectrum a, Fig. 10) shows two intense ν(OH) vibration bands: at 3745 cm$^{-1}$ with a low frequency tail, and at 3612 cm$^{-1}$ (symmetrical). The 3745 cm$^{-1}$ band is assigned to terminal silanol groups located on the external surface of the crystallites. Its strong intensity is in agreement with the high external surface measured by $N_2$ adsorption isotherms (ca. 65 m$^2$ g$^{-1}$), resulting from the small particle size (ca. 100 nm). OH groups detected in the 2D analysis around 3665 cm$^{-1}$ are visible as a very weak band. 2,4,6-collidine (equilibrium pressure $P_e = 2$ Torr) is then adsorbed at room temperature on the activated catalyst, yielding

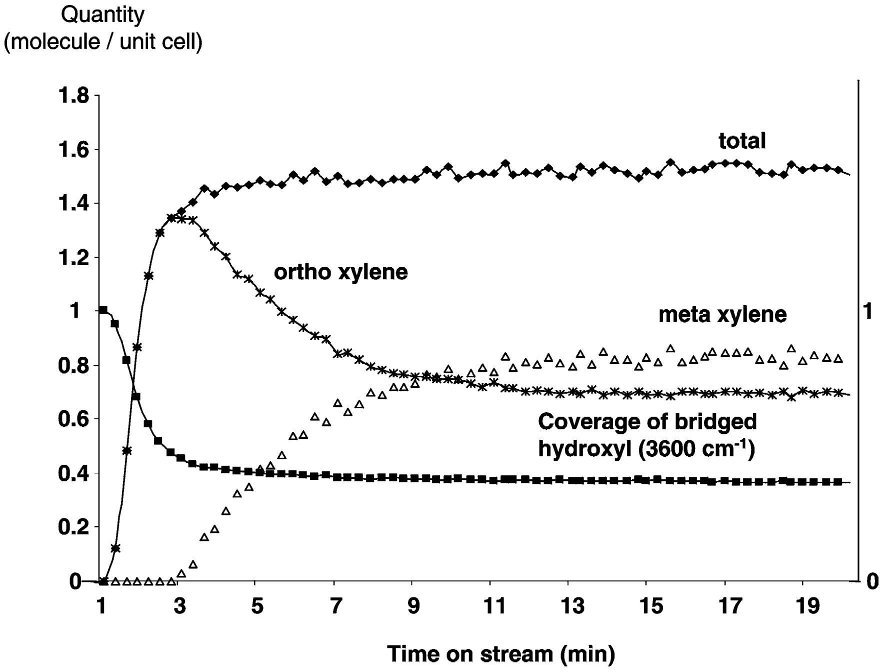

Fig. 6. Evolution of the isomers concentration in the pores at 473 K determined by infrared using bands chosen by 2D-COS.

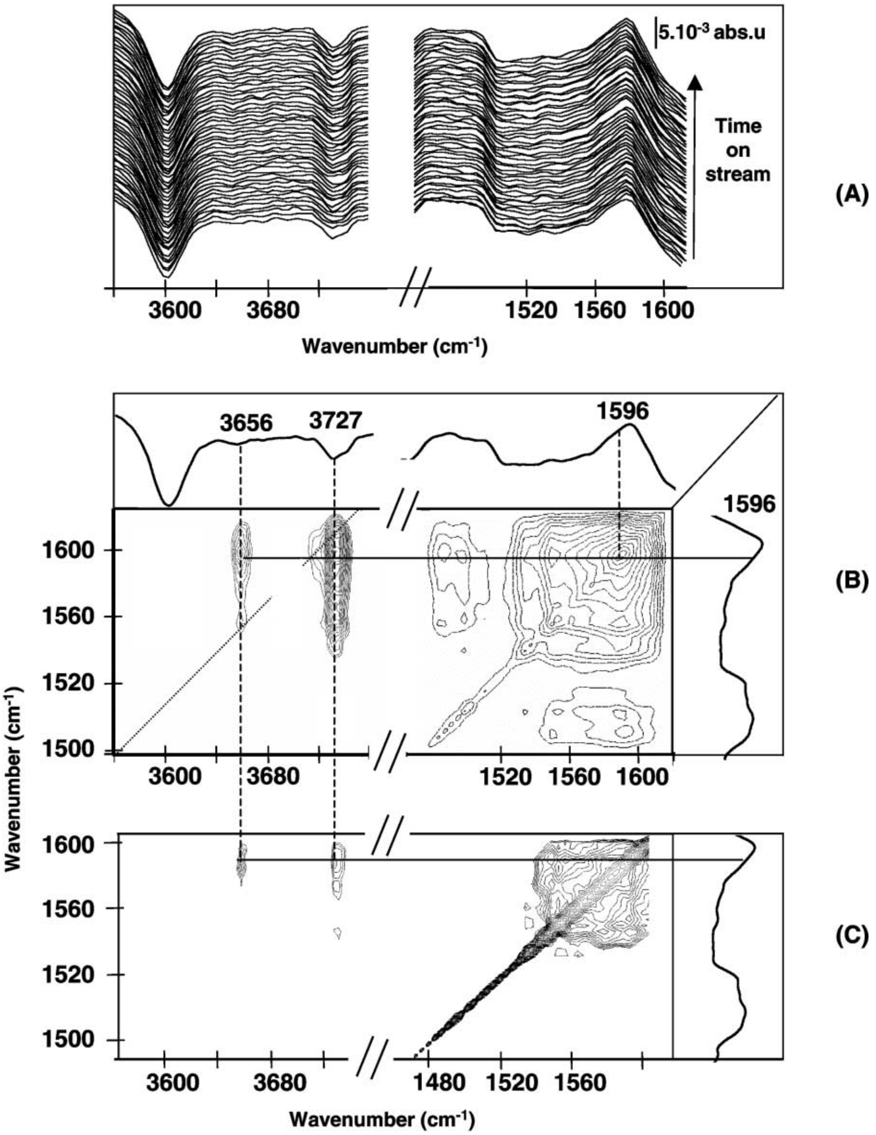

Fig. 7. (A) 1D spectra recorded during xylene isomerisation at 573 K on H-MFI in steady-state, after initial equilibration time (188 spectra, 5–60 min). (B) Right: positive covariance analysis of the 1360–1650 cm$^{-1}$ region. A large covariance peak centred at 1596 cm$^{-1}$ was detected; it could not be assigned to a xylene isomer. The weak signal to noise ratio in the direct spectra did not allow its observation without 2D-COS. Left: negative covariance analysis of the same series between the band at 1596 cm$^{-1}$ and the $\nu$(OH) region. Although adsorbed *meta*-xylene led to the band at 1600 cm$^{-1}$, the maximum negative correlation was observed at 1596 cm$^{-1}$. It should be noted that the perturbation of the acidic sites ($\nu$(OH) at 3600 cm$^{-1}$) was not linked to the perturbations described here. The spectra on the axes are not normal 1D spectra, they are mean spectra of the series, only displayed to ease understanding. (C) Regions of the 2D map for which the absolute value of the correlation coefficient is superior to 0.8.

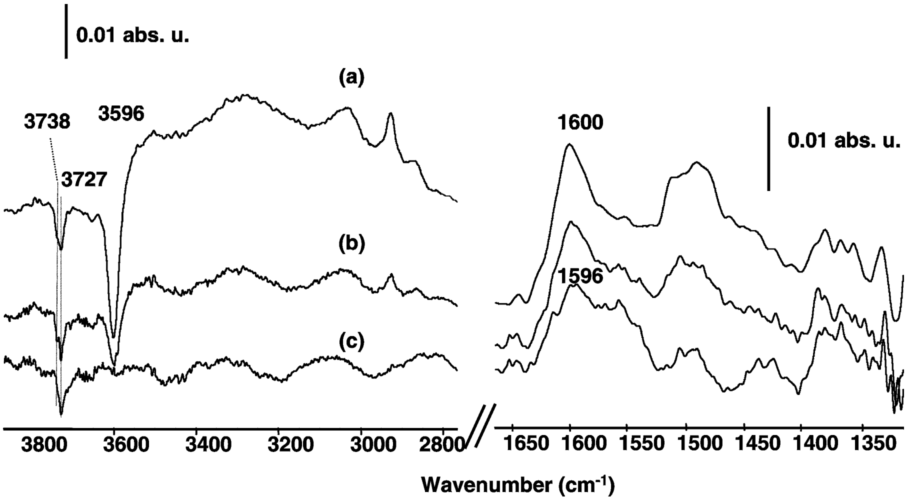

Fig. 8. Infrared spectra of MFI at 573 K after 60 min on stream (a), evacuation on pure helium 5 min (b), and 60 min (c).

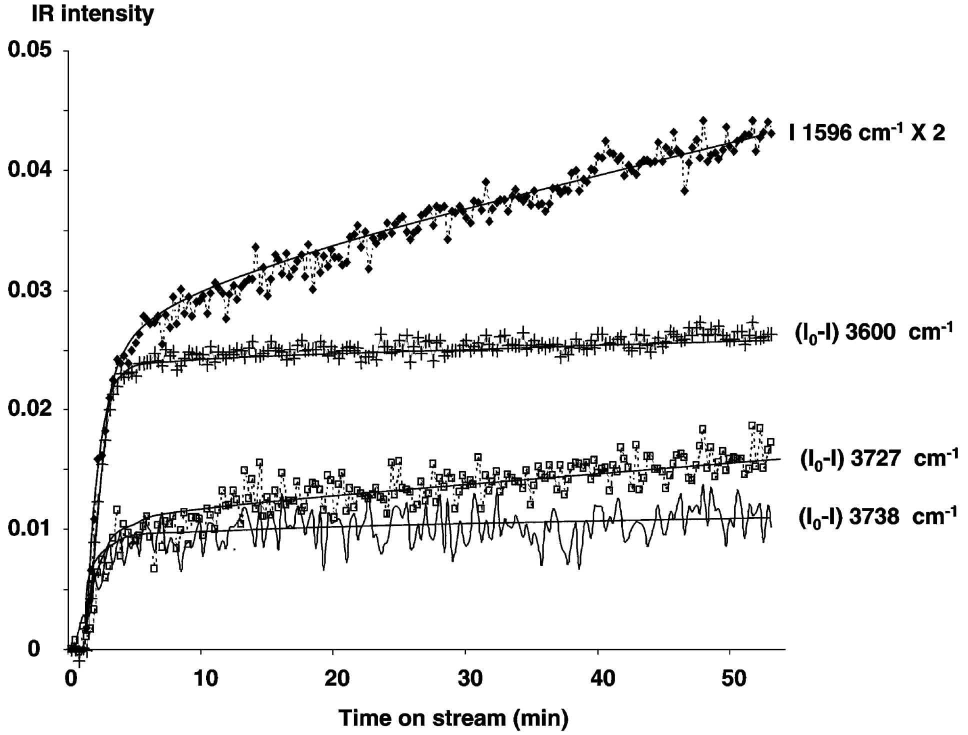

Fig. 9. Intensity changes for the OH and coke bands (detected by 2D-COS) during the reaction at 573 ($I_0$ is the intensity at time 0).

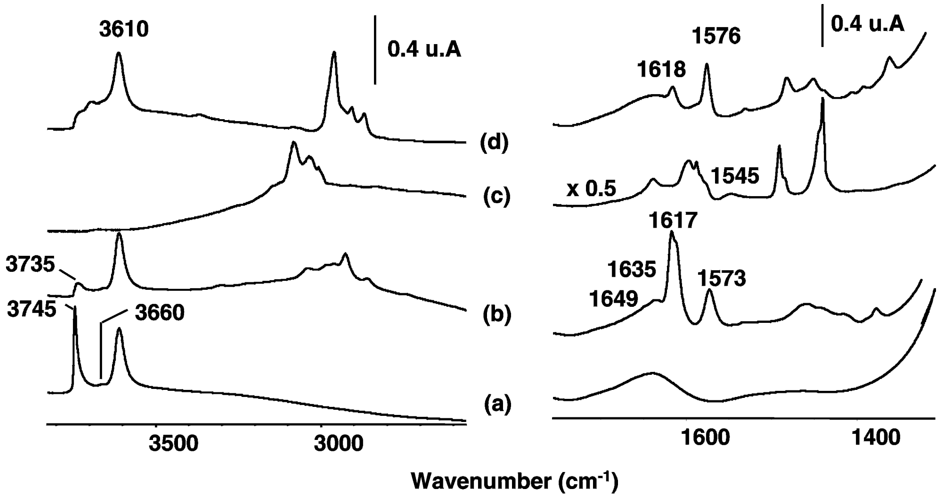

Fig. 10. Infrared spectra of activated MFI (a), after introduction of 2,4,6-collidine (b), pyridine (c), and DTBP (d).

spectrum b (Fig. 10). The 3612 cm$^{-1}$ band is not affected by collidine, indicating that this molecule does not reach the bridged OH groups. The silanol band at 3745 cm$^{-1}$ totally disappears, these OH groups interact with the bulky probe. Under this formerly intense external silanol band, we can now see a low frequency asymmetric component at 3735 cm$^{-1}$.

DTBP is another probe used to differentiate acid sites on the external surface of 10-MR pore zeolites [19]. We obtained the same result with collidine as with DTBP adsorption (Fig. 10, spectrum d), which indicates that collidine is also too bulky to enter the channels of MFI zeolites. However, in our experiments, collidine has two main advantages over DTBP. First, collidine is easier to handle in the vacuum line due to its higher vapour pressure; it does not contaminate the cell as much as DTBP. Second, the infrared spectrum of collidine is clearer in the $\nu$(OH) region below 3720 cm$^{-1}$ than that of DTBP. In the spectrum of DTBP, a broad band with an intense shoulder at 3700 cm$^{-1}$ (probably due to the $\nu$(OH) vibration band of silanol groups interacting with tertio-butyl groups) prevents the detection of weak bands in this region.

Upon introduction of 5 Torr of pyridine in the cell at room temperature on the activated catalyst, all $\nu$(OH) bands between 3750 and 3600 cm$^{-1}$ disappear (spectrum c, Fig. 10), indicating that the OH groups corresponding to the 3735 and 3612 cm$^{-1}$ bands can be reached by pyridine but not by collidine. This allows the unambiguous location of the MFI OH groups: most of the silanol groups (3745 cm$^{-1}$) are located on the external surface of the crystallite, but a minor part of the silanol groups (3735 cm$^{-1}$) as well as the Brønsted acid sites (3612 cm$^{-1}$) are located mainly inside the pores. As seen on the difference spectrum a − b (only displayed in Fig. 12 for sake of clarity) the silanol band at 3745 cm$^{-1}$ which is perturbed by collidine is asymmetrical, and contains a small component at 3735 cm$^{-1}$, also affected by collidine adsorption. This points to the location of a small portion of these low frequency silanols on the external surface. Pyridine is completely desorbed from these silanols after evacuation at 443 K, and these OH groups are therefore not acidic.

### *4.3.2. Assignment of bands of adsorbed collidine (Fig. 11)*

Substituted pyridines produce specific infrared signals for their interaction with Lewis sites, or with strong or weak Brønsted sites. These interactions can be identified in the aromatic ring vibration region. In order to assign the IR bands of collidine and to know its potential as an acidity probe, collidine is adsorbed on silica, gamma alumina and an HY zeolite sample.

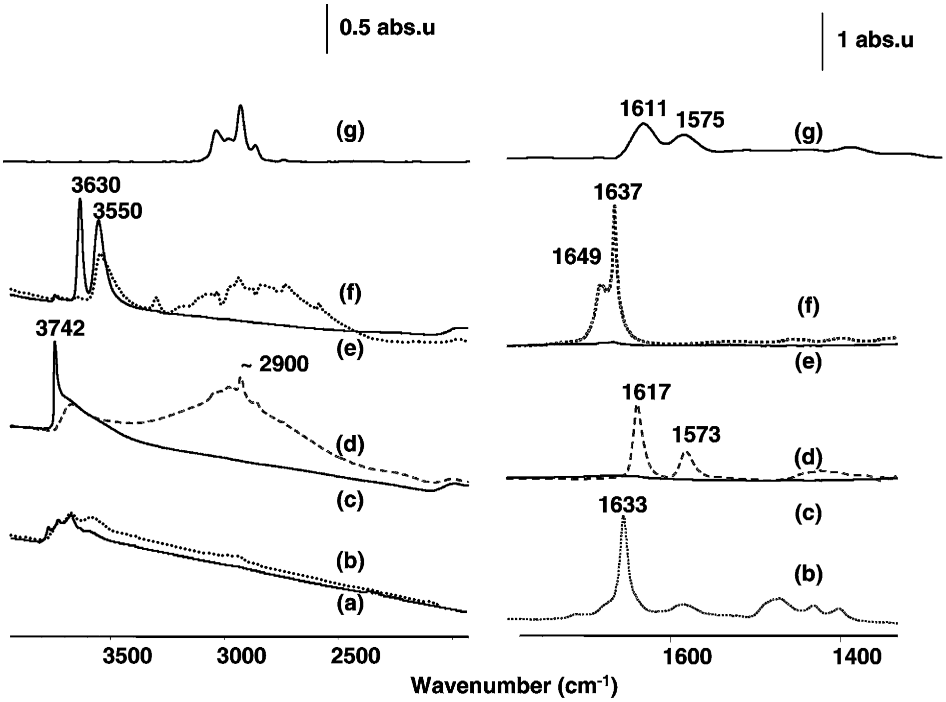

Fig. 11. Infrared spectra of alumina, silica and HY after activation (spectra a, c, f, respectively) and collidine adsorption (spectra b, d, e, respectively). Infrared spectrum vapour phase of 2,4,6-collidine (spectrum g).

On activated gamma alumina (673 K, 6 h), adsorption of collidine and its evacuation at 473 K leads to an intense band at 1633 cm$^{-1}$ (spectra a and b, Fig. 11) which we assign to collidine coordinated to Lewis sites.

After introduction of 0.5 Torr collidine on a silica sample (activated under vacuum at 673 K for $4\frac{1}{2}$ h), perturbation of the silanol bands between 3742 and 3700 cm$^{-1}$ is clear (spectra c and d, Fig. 11). An H-bond is indicated by the presence of perturbed $\nu$(OH) vibration bands at 2800–2900 cm$^{-1}$. In the region of cycle vibrations, bands are observed at 1573 and 1617 cm$^{-1}$. The latter band is shifted from its position observed in the vapour phase at 1611 cm$^{-1}$ (spectrum g), and is thus typical for collidine H-bonded to silanol groups.

Our HY zeolite sample contains only Brønsted sites [8]. After adsorption of collidine (0.5 Torr, 425 K) and evacuation (573 K) to eliminate physisorbed species, high frequency OH groups ($OH_{HF}$), the most acidic on this catalyst, are totally perturbed and the $\nu(OH_{HF})$ band at 3630 cm$^{-1}$ completely disappears (spectra e and f, Fig. 11). Adsorbed species then lead to two intense bands at 1637 and 1649 cm$^{-1}$, which we assign to the protonated form of collidine.

On our MFI sample, the perturbation of the external silanol groups (which frequency is the same as that of isolated Si–OH on silica [19]) results in a broad band at ca. 2900 cm$^{-1}$, similar to what we observed on silica, and associated to hydrogen-bonded collidine bands at 1573 and 1617 cm$^{-1}$. Weak bands at 1635 and 1649 cm$^{-1}$ associated to collidinium species reveal the presence of a small number of Brønsted sites accessible to collidine. As far as the 3665 cm$^{-1}$ band is concerned, its very weak intensity does not permit to clearly determine the effect of the collidine adsorption and its location. This band is assigned to extra framework Al–OH [20], its intensity increasing after a mild hydrothermal treatment [21].

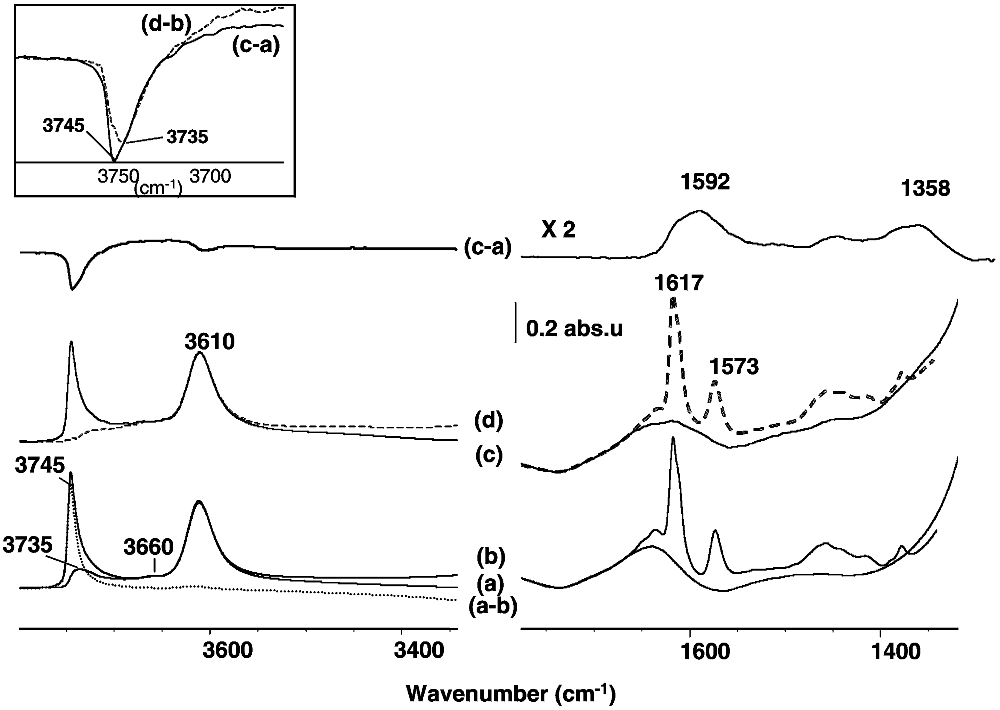

Fig. 12. Infrared spectrum of the fresh (a, activated and b, with adsorbed collidine) and coked sample (by heating with 15 Torr of cyclohexene at 623 K for 10 h and evacuation at 623 K; c, as such and d, with adsorbed collidine). The difference spectrum c − a shows the perturbation of the surface by coke, and d − b shows silanol groups perturbed by coke but inaccessible to collidine.

### *4.3.3. Probes adsorption: comparison between fresh and coked H-MFI (Figs. 12 and 13)*

Only trace amounts of coke are formed during xylene isomerisation on H-MFI. In order to study coked H-MFI in a quartz infrared cell, we elected to reproduce the coking of the sample using cyclohexene, by heating the catalyst in the presence of 15 Torr cyclohexene at 623 K for 10 h in the infrared cell. Two broad bands are clearly visible at 1592 and 1358 $\mathrm{cm}^{-1}$ after evacuation (spectrum c – a, Fig. 12), indicating the formation of a carbon deposit similar to the one observed on other zeolites under the same coking conditions [5–8]. Bridged OH band is only very weakly perturbed. However, a silanol peak with a main band at 3745 $\mathrm{cm}^{-1}$ and a strong component at 3735 $\mathrm{cm}^{-1}$ are clearly affected. The comparison of the two spectra obtained upon collidine adsorption before and after coking of the catalyst (spectrum d − b, Fig. 12) shows that coke deposits affect only those of the silanol groups at 3735 $\mathrm{cm}^{-1}$ that are inaccessible to collidine. The coke deposit, hence, corresponds mainly to the perturbation of silanol OH groups located inside the micropores. A small fraction of the SiOH band at 3745 $\mathrm{cm}^{-1}$ is, however, perturbed by coke, indicating the formation of a small amount of coke on the external surface of the crystallites. The small part of Brønsted sites accessible to collidine are not affected by the coke deposit.

Pyridine adsorption at room temperature (5 Torr) on the activated and the coked samples leads in both cases to the total disappearance of $\nu$(OH) bands between 3750 and 3600 $\mathrm{cm}^{-1}$ (spectra b and e, Fig. 13). Coke, hence, does not block the access of pyridine to OH groups. The intensity of the 1545 $\mathrm{cm}^{-1}$ band for protonated pyridine is the same on the fresh and coked samples, coke formation consequently does not perturb the Brønsted acidity of the catalyst. We have seen previously by pyridine adsorption that the silanol groups at 3735 $\mathrm{cm}^{-1}$ (here perturbed by coking) are indeed not acidic.

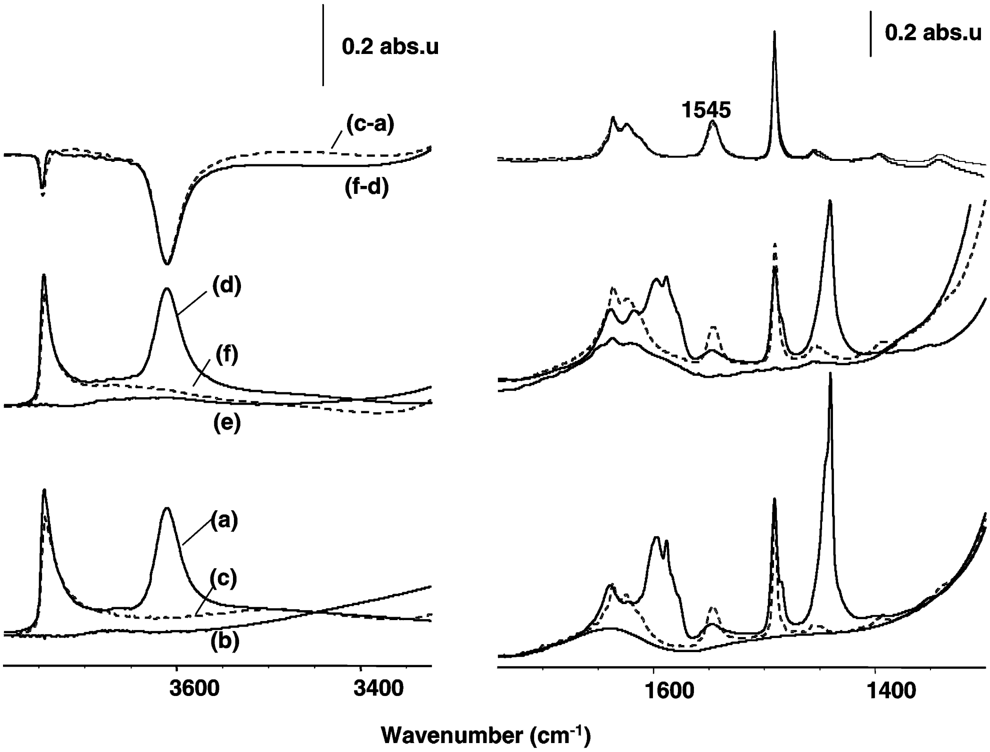

Fig. 13. Infrared spectrum of the fresh (a, activated; b, with adsorbed pyridine at $P_e = 5$ Torr, and c, after subsequent evacuation at 443 K) and coked sample (by heating with 15 Torr of cyclohexene at 623 K for 10 h and evacuation at 623 K; d, as such; e, with adsorbed pyridine at $P_e = 5$ Torr and f, after subsequent evacuation at 443 K). The difference spectra show the perturbation of the surface by pyridine: c − a on the fresh sample, and f − d on the coked sample.

## 5. Conclusion

2D-COS analysis is a powerful technique for the in situ characterisation of surface species on a working catalyst. Coke formation during xylene isomerisation is particularly well-evidenced and the relationship between coke formation and the perturbation of specific OH groups is clearly observed on 2D graphs, while it could hardly be detected on normal 1D infrared spectra. The speed of modern personal computers together with an adequate software makes 2D-COS a fast and convenient tool, giving precious help for data analysis, often a tedious task given the great number of spectra collected in time-resolved experiments. Such data treatment methods should in the near future facilitate detailed microkinetic descriptions of catalytic surfaces, even with complex adsorbed systems.

Infrared data obtained on the working catalyst have been completed by a more comprehensive study of the catalyst in a static infrared cell. Use of collidine as a probe molecule for the external surface of MFI zeolites is validated. Together with pyridine, this probe gives information on the location of various OH groups in the structure, as well as on the location of carbonaceous deposits formed during hydrocarbon conversion reactions. Under the experimental conditions of this study, irreversibly adsorbed carbonaceous deposits denoted as coke, neither perturb bridged OH groups nor Brønsted acidity in MFI, whether these are located in the micropores or on the external surface with a very low concentration.

Coke in MFI zeolite perturbs silanol groups associated with a band at 3735 $cm^{-1}$, although pyridine adsorption indicates these OH groups are not strongly acidic. Contrarily to silanols associated with the

3745 cm$^{-1}$ band, which are located on the external surface of the crystallites, silanols at 3735 cm$^{-1}$ are mainly located inside the micropores. The silanol groups perturbed by coke deposition are preferably located inside the micropores. This coke deposit presents infrared bands similar to the ones observed on other zeolites in similar coking conditions [14,22]. On BEA and Y zeolites, however, coke bands are much more intense and bridged acidic OH groups are clearly affected. The smaller size of the channels in MFI zeolite limits bimolecular reactions, necessary for the formation of coke. The silanol groups in the micropores indicate the presence of local defects in the framework, and the preferred location of coke on these defects rather than on bridged OH groups might be linked to less important steric constrains in these defects. The band at 3665 cm$^{-1}$ is also affected by coke deposit during *ortho*-xylene conversion. This band is too weak in the sample activated under very mild condition to determinate a possible perturbation by a probe molecule. However, coking and collidine adsorption experiments on a steamed MFI sample (to obtain a more intense IR band at 3665 cm$^{-1}$) could be interesting to study the influence of coke species on these hydroxyl groups and obtain the best location of these in the structure.

## Acknowledgements

The authors are grateful to Dr. A. Travert for discussions and references on collidine adsorption, Dr. J.M. Goupil and Prof. C. Fernandez for discussions, and Dr. J.C. Lavalley for his continuous support and valuable suggestions.

## References

[1] H. Günther, NMR Spectroscopy: Basic Principles, Concepts and Applications in Chemistry, Wiley, Chichester, UK, 1994.
[2] I. Noda, A.E. Dowrey, C. Marcott, Mikrochim. Acta (Wien) 1 (1988) 101.
[3] I. Noda, Appl. Spectrosc. 47 (1993) 1329.
[4] J.F. Joly, N. Zanier-Szydlowski, S. Colin, F. Raatz, J. Saussey, J.C. Lavalley, Catal. Today 9 (1991) 31.
[5] S. Jolly, J. Saussey, J.C. Lavalley, N. Zanier, E. Benazzi, J.F. Joly, in: Proceedings of the Ninth IZC, Vol. II, 1992, 1993, p. 319.
[6] S. Jolly, J. Saussey, J.C. Lavalley, N. Zanier, E. Benazzi, J.F. Joly, Ber. Bunsenges. Phys. Chem. 313 (1993) 97.
[7] J. Jolly, J. Saussey, J.C. Lavalley, J. Mol. Catal. 86 (1994) 401.
[8] J.C. Lavalley, S. Jolly, A. Janin, J. Saussey, Mikrochim. Acta 14 (1997) 51.
[9] F. Le Peltier, P. Chaumette, J. Saussey, M.M. Bettahar, J.C. Lavalley, J. Mol. Catal. A 132 (1) (1998) 91.
[10] A. Vimont, O. Marie, J.P. Gilson, J. Saussey, F. Thibault-Starzyk, J.C. Lavalley, Stud. Surf. Sci. Catal. 126 (1999) 147.
[11] F. Poignant, J.L. Freysz, M. Daturi, J. Saussey, J.C. Lavalley, Stud. Surf. Sci. Catal. 130 (2000) 1487.
[12] C. Lagrange-Garrigou, J.M. Lebas, M.L. Josien, Spectrochim. Acta 12 (1958) 305.
[13] G. Mirth, J. Čejka, J. Lercher, J. Catal. 139 (1993) 24.
[14] H.G. Karge, W. Niessen, H. Bludau, Appl. Catal. A 146 (1996) 339.
[15] C. Otero Areán, E. Escalona Platero, M. Pañarroya Mentruit, M. Rodriguez Delgado, F.X. Llabrès I Xamena, A. Garcia-Raso, C. Morterra, Micropor. Mesopor. Mater. 34 (2000) 55.
[16] C. Otero Areán, M. Rodriguez Delgado, M. Pañarroya Mentruit, X.F. Llabrès I Xamena, C. Morterra, Stud. Surf. Sci. Catal. 130 (2000) 3137.
[17] M. Trombetta, T. Armaroli, G.A. Alejandre, R.J. Solis, G. Busca, Appl. Catal. A 192 (2000) 125.
[18] A. Corma, V. Fornes, L. Forni, F. Marquez, J. Martinez-Triguero, D. Moscotti, J. Catal. 179 (1998) 451.
[19] A. Burneau, J.P. Gallas, in: A.P. Legrand (Ed.), The Surface Properties of Silicas, Wiley, New York, 1998, p. 147.
[20] E. Loeffler, U. Lohse, C. Peuker, G. Oehlmann, L.M. Kustov, V.L. Zholobenko, V.B. Kazansky, Zeolites 266 (1990) 10.
[21] M.S. Campbell, D.M. Bibby, J.M. Coddington, R.F. Howe, R.H. Meinhold, J. Catal. 338 (1996) 161.
[22] A. Vimont, F. Thibault-Starzyk, J.C. Lavalley, Stud. Surf. Sci. Catal. 130 (2000) 2969.