

2D correlation IR spectroscopy of xylene isomerisation on H-MFI zeolite

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Received (in Oxford, UK) 10th March 2000, Accepted 26th April 2000

Published on the Web 22nd May 2000

2D correlation IR spectroscopy (2D-COS) allows quantitative monitoring of xylene isomers in the pores of H-MFI zeolite under working conditions; coke bands invisible in the direct spectra are detected, indicating traces of coke localised on specific OH groups.

IR spectroscopy is nowadays used routinely for the study of the surface of working heterogeneous catalysts in catalytic reactors equipped with IR transparent windows. It has, for example, been applied to xylene isomerisation in zeolites.¹ The main difficulty resides in the complexity of the spectra, and in the choice of adequate bands for the characterisation and quantification of species of interest. Detection of trace compounds is often a problem because of the low signal to noise ratio obtained at high temperatures in the IR cell. New data treatment methods such as 2D correlation IR spectroscopy (2D-COS) have led to significant improvements in this area.^{2,3} We report here, the application of 2D-COS to the *in situ* IR study of *o*-xylene isomerisation in H-MFI zeolite under working conditions. This led to an improvement in the quantitative monitoring of xylene isomers in the micropores of the solid and to the detection of traces of coke in the catalyst. A correlation was found between the degree of coke incorporation and the perturbation of specific hydroxy groups in the solid.

Experiments were performed in a microreactor-IR cell already described elsewhere,⁴ in which the spectra of both the self supported wafer of the catalyst and the adsorbed species can be recorded during the reaction up to 725 K. A nitrogen gas stream was diverted to a saturator filled with *o*-xylene and maintained at a constant temperature (300 K) and the resulting mixture fed to the reactor/IR cell. The reaction conditions were: 473–573 K, 8 Torr *o*-xylene partial pressure, WHSV: 2.7 h⁻¹. The reaction products exiting the reactor were analysed by gas chromatography. The spectrometer was a Nicolet Magna 750, used at 2 cm⁻¹ resolution (Happ-Genzel apodisation function).

The spectrum of the activated zeolite at 473 K shows in the ν(OH) stretching vibration region two intense bands at 3738 and 3602 cm⁻¹, assigned to the stretching vibrations of silanols and acidic bridged hydroxy groups, respectively. Upon *o*-xylene adsorption at this temperature, the intensities of both bands immediately decreased. Attenuation is moderate for the silanol band (10%), indicating only a weak interaction. By contrast, the intensity decrease of the acidic hydroxy band is much more substantial (70% reduction) and can be assigned to the formation of hydrogen bonds with the aromatic molecule. The perturbed OH leads to a broad band centred at 3200 cm⁻¹. At the same time, a complex group of bands appears between 1380 and 1600 cm⁻¹, assigned to vibrations of the adsorbed *o*-xylene. During the first few minutes of reaction, a new band appears at 1605 cm⁻¹, assigned to the ν_{sa} or ν_{sb} vibration of *m*-xylene (1610 cm⁻¹ in the liquid phase). Although *p*-xylene should exhibit an intense and characteristic band (1515 cm⁻¹ in the liquid phase), this is not observed on the surface, although *p*-xylene is present in the reaction products (GC analysis). This is 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).

2D-IR spectroscopy was introduced by Noda *et al.*,² and was

initially based on time resolved IR spectroscopy of a sinusoidal perturbation such as that produced by the mechanical strain of a vibrating polymer. Noda later proposed to generalise his method to non-sinusoidal perturbations such as irradiation or electrochemical perturbations,³ leading to significant increases in sensitivity and resolution of complex band groups. Here, we consider the chemical reaction as the perturbation. We used 2D-COS analysis of a series of spectra recorded between 4 and 14 min reaction time in the *o*-xylene isomerisation reaction to resolve the aromatic vibration bands (Fig. 1).

2D-COS allows analysis of spectral changes with time. Spectra can be obtained either by a Fourier transform of the interferograms recorded at regular time intervals, or by a simple covariance analysis in the spectral series, by use of eqn. (1)

$$\text{COV}(v_1, v_2) = \frac{1}{N} \sum_{i=1}^{i=N} [A_i(v_1) - \bar{A}(v_1)][A_i(v_2) - \bar{A}(v_2)]$$

$$r(v_1, v_2) = \frac{\text{COV}(v_1, v_2)}{\sigma_{v_1} \sigma_{v_2}} \quad (1)$$

where N is the total number of spectra recorded, $A_i(v_1)$ the absorbance at v_1 for the i th spectrum, $\bar{A}(v_1)$ the absorbance at v_1 for the reference spectrum and $r(v_1, v_2)$ the correlation coefficient between intensities at wavenumbers v_1 and v_2 . The reference spectrum is generally the arithmetic mean spectrum but the first spectrum or the spectrum at steady-state can also be used. σ_{v_1} , σ_{v_2} are the standard deviations at v_1 and v_2 , respectively. A 2D display of the covariance or correlation between all frequencies in the spectrum gives information on the relationship existing between various bands, depending on their simultaneous or independent intensity variations. In the following, we elect to split the graphical display into two separate sets for positive and negative covariance, to identify bands varying in the same way (positive covariance, Fig. 2) or in opposite ways (negative covariance, not shown). During isomerisation, *o*-xylene is progressively replaced by *m*-xylene which accumulates in the pore system. A negative correlation

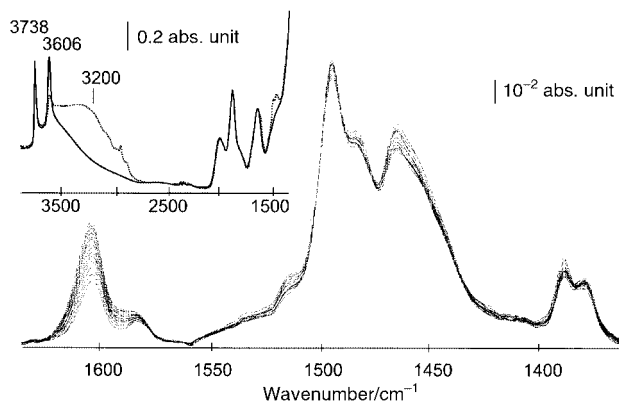


Fig. 1 Some spectra recorded between 4 and 14 min reaction time at 473 K. Inset: spectra of the clean catalyst (—) and of the catalyst under working conditions (.....).

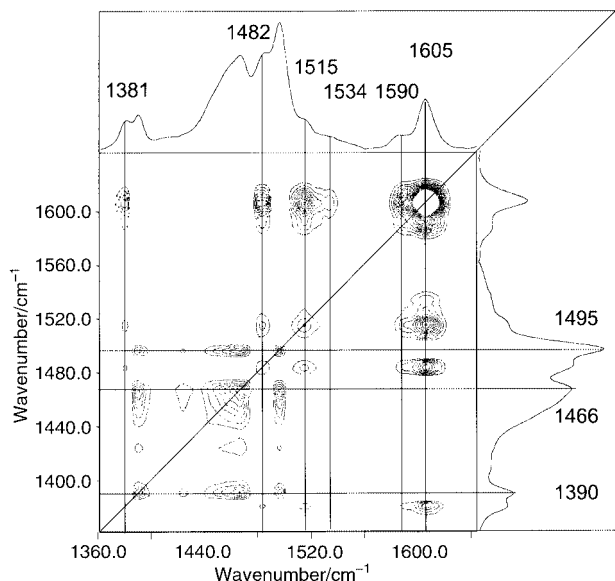


Fig. 2 2D positive covariance map obtained with 34 spectra recorded between 4 and 14 min reaction time at 473 K. The spectra shown on the axes are the mean spectra in the series.

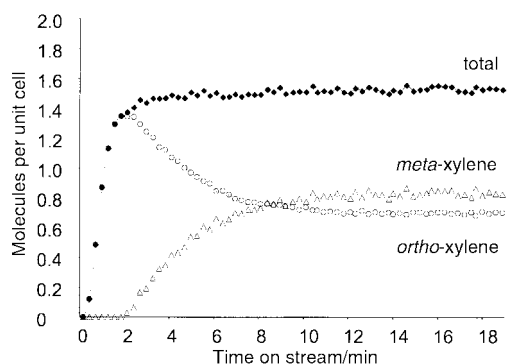


Fig. 3 Concentration of isomers in the pores at 473 K determined by IR using bands studied by 2D-COS.

should therefore appear between the *o*-xylene bands (whose intensities decrease) and the *m*-xylene bands (whose intensities increase). On the other hand, bands having contributions from *o*-xylene are autocorrelated, as are bands having contributions from *m*-xylene. Assignment of bands is thus considerably eased. Additionally, it was possible to detect very weak bands which are invisible in the normal 1D spectra. At 473 K, *m*-xylene bands occur at 1605, 1590, 1535, 1515, 1482 and 1381 cm^{-1} , and *o*-xylene bands are at 1495, 1466, 1458, 1423, 1412 and 1390 cm^{-1} . The regions exhibiting the most intense negative correlation were chosen for the *in situ* quantitative monitoring: 1605 cm^{-1} for *m*-xylene and 1466 cm^{-1} for *o*-xylene. Approximate extinction coefficients for these two bands were determined by adsorbing the two pure isomers on the catalyst at 400 K (highest temperature achievable without isomerisation) under the same conditions in the IR cell and in a thermogravimetric MacBain balance. The obtained values were $\epsilon_{1605} = 0.026 \pm 0.004 \text{ cm } \mu\text{mol}^{-1}$ and $\epsilon_{1466} = 0.029 \pm 0.004 \text{ cm } \mu\text{mol}^{-1}$. The IR intensities of these two bands can be used to measure the concentrations of the isomers in the pore system and their change with time on stream (Fig. 3).

2D-COS is particularly powerful when applied to spectra recorded at higher temperature, with low signal to noise ratio, during the reaction at 573 K. When the steady state is reached after the initial adsorption step, no change is observable in the 1D spectra, but 2D-COS clearly shows a cross-peak in the region of aromatic vibrations at 1596 cm^{-1} (Fig. 4, left). A very weak band is found at this wavenumber in the 1D spectra, which is masked by overlapping xylene bands. The negative covari-

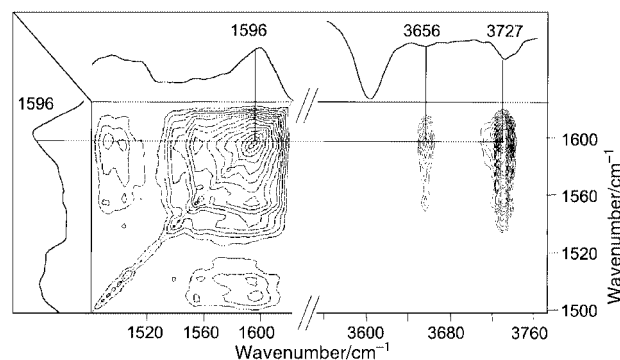


Fig. 4 Left: positive covariance analysis of the 1360–1650 cm^{-1} region during isomerisation at 573 K (188 spectra, 60 min). A large covariance peak centred at 1596 cm^{-1} was detected which could not be assigned to a xylene isomer. The weak signal to noise ratio in the direct spectra did not allow its observation without 2D-COS. Right: negative covariance analysis of the same series of spectra between the band at 1596 cm^{-1} and the $\nu(\text{OH})$ region. Although adsorbed *m*-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 [$\nu(\text{OH})$ at 3600 cm^{-1}] was not linked to the perturbations described here. The spectra on the axes are not normal 1D spectra, but are mean spectra of the series which are displayed for clarity.

ance map between the region of aromatic vibrations and $\nu(\text{OH})$ bands (Fig. 4, right) indicates a link between the 1596 cm^{-1} band and a decrease of the intensity of two bands located at 3727 and 3656 cm^{-1} assigned to low frequency silanols and to extraframework AlOH groups, respectively.⁵ By flushing the catalyst surface with pure helium at the reaction temperature, adsorbed xylenes are eliminated, and the corresponding bands disappear. A species, however, remains adsorbed on the surface, and is characterised by a band at 1596 cm^{-1} . Additionally $\nu(\text{OH})$ bands are not completely recovered, and (very) weak negative bands appear in the difference spectrum at 3727 and 3656 cm^{-1} . These correspond to the perturbation of the low wavenumber silanols and of the extraframework AlOH groups detected in the course of the reaction by 2D-COS. We interpret this result in terms of traces of coke (bands around 1600 cm^{-1} are generally observed after coke formation on zeolites in hydrocarbon conversion reactions),^{6,7} localised on these specific silanol and AlOH groups, but not on the acidic (bridged OH) sites. Coke is only present in trace amounts and the activity remains constant throughout the reaction. A slight increase in *para*-selectivity is however observed by GC analysis of the products. Unambiguous determination of the localisation of these OH groups in the microporous structure is currently in progress.

2D-COS treatment of the spectra is therefore a powerful new technique; it enables a much more detailed analysis of IR spectra, in particular for the monitoring of the working catalyst. Non-interfering bands can be chosen for the quantitative measurement of surface species under reaction conditions at 473K. At higher temperature (lower signal to noise ratio), traces of coke can be detected on H-MFI zeolite, linked to the perturbation of specific OH groups (not those of the acidic sites).

Notes and references

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