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Spatially resolving infrared spectroscopy for parallelized characterization of acid sites of catalysts via pyridine sorption: Possibilities and limitations

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Abstract

A new high-throughput analysis setup has been developed to investigate the acidity of up to eight solid materials in a parallel way. This method applies an IR focal plane array detector and an especially designed measurement cell adapted to this system. The whole system was validated by using zeolite Y, H-ZSM-5, and H-Mordenite as acidic materials and amorphous silica as nonacidic material. It was found that with zeolite Y and H-ZSM-5 it is possible to get IR spectra of the adsorbed pyridine with comparable quality as that in a conventional setup. By heating the samples in the measurement cell it is possible to follow the desorption of the adsorbed pyridine to distinguish different adsorbed pyridine species on the surface. For amorphous silica only physisorbed pyridine has been found and after heating of the sample there was no pyridine left. In contrast to this it was not possible to analyze the acid sites of H-Mordenite with this setup. This could be due to scattering effects caused by the particle size of the material which has a severe influence on the feasibility of measurements in this setup. Also other adsorptives could be used in this cell to analyze different surface properties.

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1. Introduction

High-throughput experimentation (HTE) techniques in the field of heterogeneous catalysis have entered the laboratories toward the end of the 1990s [1–3]. Various different methods have been developed to automate synthesis of materials [4–7], parallelize catalytic testing [8–11], and accelerate product analysis [12–22]. In a relatively short time frame these techniques have widely spread and are now acknowledged to accelerate catalysis research, even if there are still some reservations. This assessment holds for the discovery of new materials with unknown properties as well as for optimizing existing catalysts.

High-throughput characterization, on the other hand, is substantially less developed. XRD using a spatially resolving diffractometer was the first technique introduced for the phase analysis of solid libraries [5,23]. However, bulk structure analysis is often not the most suitable technique for characterizing a solid catalyst. In order to better understand why certain members of a catalyst library perform better than others, high-throughput analysis techniques for analyzing the surface properties of solids are also needed.

One of the most suitable techniques for studying the surface of solids is IR spectroscopy using probe molecules. In principle, this technique could be parallelized, for instance, by using an FTIR microspectrometer in combination with an xy-sample chamber. However, all our attempts to use this technique were not very promising: For a proper analysis of surface sites, the spectrum of the catalyst without adsorbed probe molecules needs to be subtracted. This, however, requires the analysis of exactly the same spot of the sample with and without adsorbed probe molecules. This exact repositioning of the sample, typically powders which can shift, has been proven to be extremely demanding. We therefore abandoned this line of development and made use of a more recent development, the focal plane array IR detectors, which allow IR spectra with high spatial resolution to be recorded. Pioneering work in this field was carried out by the group of Lauterbach. They used a FPA system to observe the adsorption of carbon monoxide on the surface of Cu-ZSM-5 and platinum on silica, respectively [24].

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Table 1
Classification of chemi- and physisorbed pyridine on acidic solids

Position of band [cm^{-1}]	Classification	Linkage of pyridine
1638	ν [CC(N)]	Brønsted acid sites
1620	ν [CC(N)]	Lewis acid sites
1580	ν [CC(N)]	Physisorbed
1545	ν [CC(N)]	Brønsted acid sites
1490	ν [CC(N)]	Brønsted and Lewis acid sites
1450	ν [CC(N)]	Lewis acid sites
1439	ν [CC(N)]	Physisorbed

For catalysis research there are other, even more challenging problems with regard to surface analysis of solid materials. Surface acidity is one of the key properties of many catalytic materials which are used in various processes, ranging from fine chemical production to large-scale petrochemical processes. Hence, suitable analysis techniques have been developed [25,26]. A prevalent method is based on the different vibration bands of pyridine, which is chemisorbed on the acid sites of a solid material. This effect was first described for the determination of surface acidity by Parry [27]. With pyridine as probe molecule it was furthermore possible to differentiate between Brønsted and Lewis acid sites (Table 1) [28].

Analysis of acidity with adsorbed pyridine, however, is a rather lengthy procedure. First the samples must be outgassed at elevated temperatures under high vacuum conditions, and then the background spectra are recorded. After equilibration of pyridine, the samples must be treated at elevated temperatures to remove physisorbed pyridine, and finally the spectrum of adsorbed pyridine is recorded. Optionally, desorption at different temperatures can also be added to the program in order to obtain information on the strength of acid sites. Finally, the cell must be outgassed again in order not to compromise the analysis of the next sample. A full analysis of the acidity including all steps may thus take a full day. Acidity analysis using adsorbed pyridine would thus strongly benefit from a parallelization of the method. In the following we describe, how a FPA detector setup with a specially designed cell can be used to perform such analysis, and where the limitations of the technique are.

2. Experimental

2.1. Samples

Three different types of zeolites have been used for measurements. Na-Y was supplied by Degussa AG (Charge: 961/3 with SiO_2/Al_2O_3 ratio of 5.4). The Na form was ion exchanged two times with 1 mol/L NH_4NO_3 solution and then dried at 80 °C for 6 h. After drying the sample was calcined at 550 °C for 3 h. NH_4-ZSM-5 was supplied by ALSI-PENTA Zeolithe (ALSI-PENTA SM 27). The sample was calcined at 550 °C for 3 h to convert it to the H form. Na-MOR was supplied by Zeolyst (CRV 10 A, Lot No. 1822-50). The Na form was ion exchanged two times with 1 mol/L NH_4NO_3 solution and then dried at 80 °C for 6 h. After drying the sample was calcined at 550 °C for 3 h. Pyridine for sorption measurements was supplied by Fluka.

2.2. Measurement setup

The system is based on a Step-Scan IR spectrometer (Equinox of Bruker Optics), which serves as beam source. The IR beam is directed out of an external port of the spectrometer and then spread to a wide parallel beam by an optical mirror arrangement. This spreading of the beam allows illumination of a wider area on which catalyst samples can be placed. This spread parallel beam passes the measurement cell, which will be described in the following. After the measurement cell, the beam is reflected by three conventional mirrors to be focused by an optical mirror finally onto the focal plane array detector. This focusing is necessary to project the imaged $40 \times 40\ mm^2$ area to the $4 \times 4\ mm^2$ size of the detector. On this $4 \times 4\ mm^2$ the FPA detector has 64×64 pixels. Each of these 4096 pixels can detect an entire IR spectrum of the sample. By a software routine it is possible to average those pixels that belong to one certain sample to improve the signal-to-noise ratio. Typically about 200 pixels were averaged. The FPA itself is an array of mercury–cadmium–telluride detectors, which must be cooled with liquid nitrogen.

The measurement cell consists of two CaF_2 windows with a diameter of 70 mm and a thickness of 8 mm (Fig. 1). The samples are placed between these two windows and are separated from each other by an aperture made from stainless steel to avoid cross-contamination of the samples during evacuation (zeolite powders may move during evacuation). The aperture has eight circularly arranged positions for the samples, which have the same distance to the heating elements, thus ensuring an identical temperature of the different samples. A small temperature gradient over each sample itself may exist; it is, however, identical for all samples and will be averaged by averaging the spectra of all pixels corresponding to each sample. Into the aperture 1-mm pits are millcut to assure unobstructed gas flow during evacuation and pyridine equilibration. The CaF_2 windows are framed by a ring of stainless steel with an inner diameter of 70 mm, an outer diameter of 90 mm, and 42 mm height, that presses the windows against each other, and sealed with Viton O-rings. Six heating elements with a power of $6 \times 100\ W = 600\ W$ are located in the metal ring for heating of the samples. Furthermore there is an opening in the metal ring to connect the pumping system and the pyridine supply. The pumping system consists of a rotary vane pump for preevacuation and a turbomolecular pump for the evacuation of the measurement cell. With this pumping systems it is possible to achieve 5×10^{-3} Pa inside the cell.

With this measurement cell it is possible to analyze up to eight different samples at the same time with respect to their surface acidity. In principle, the degree of paralleliza-

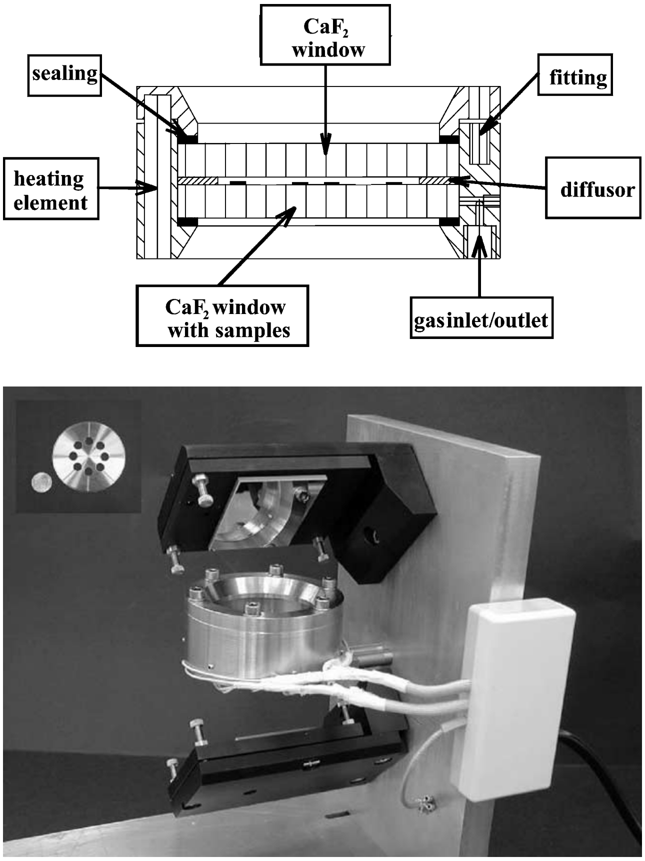

Fig. 1. Schematic drawing of the measurement cell and photograph of the measurement cell.

tion could be increased. This would be possible by the use of smaller sampling areas which would allow the accommodation of more samples on the same area. Smaller sized sampling areas have been investigated with essentially identical results. Also the area imaged (40 mm × 40 mm in the present setup) could be increased, which would require reconfiguration of the optical system. However, for the feasibility study presented here, we felt an 8-fold parallelized system to be sufficient. The cell described here is not only suitable for acidity analysis, and in principle, any appropriate adsorbent normally employed for the determination of surface properties of solid samples could be used. This may, however, require in some cases changes of construction materials or integration of low-temperature capabilities which is not a simple task. The upper temperature of the setup is at present limited by the Viton seals used, but the maximum temperature could be raised by using copper-sealed UHV flanges with CaF_2 windows without substantially redesigning the cell.

2.3. *Measurement protocol*

Samples are used as thin wafers with different thickness (see below). They are placed in the measurement cell and evacuated at room temperature for 1 h. Subsequently, the samples are evacuated at 140 °C and afterward at 250 °C to remove the water that is located on the surface and in the pore system of the zeolites. After cooling down to room temperature the background spectrum of the samples is recorded. The valves of the pumping systems are then closed and the valve of the pyridine supply is opened for 10 min. Pyridine is admitted with a pressure corresponding to its vapor pressure at room temperature, i.e., 4 mbar. The cell is subsequently evacuated again, and after 1 h of evacuation, the spectrum of adsorbed pyridine at room temperature is recorded. Physisorbed pyridine is removed by heating the cell to 200 °C for 15 min, and the next spectrum is recorded as soon as the cell is cooled down to room temperature again. Afterwards, a concluding spectrum is recorded at room temperature after the cell is heated up to 250 °C for 15 min. This is done to detect possible changes due to temperature effects.

2.4. *Conventional IR spectra*

Conventional IR spectra for comparison with the spectra taken in the parallelized setup have been recorded with a different FTIR spectrometer (Nicolet, Magna-IR 750) in a conventional high-vacuum cell for pyridine analysis. The protocol for the measurement was identical to the protocol used during analysis with the FPA detector. Samples were pressed to thin wafers of 15 mg/cm^2.

3. Results and discussion

To evaluate the novel measurement cell and the parallelized method, commercially available zeolites have been analyzed with respect to their acidity. All parallelized pyridine sorption measurements have been carried out under identical conditions.

Scattering can be a severe problem in the analysis of zeolitic materials, depending on particle size and particle morphology. This typically leads to unspecifically sloping baselines in the spectra. During the examination of different materials with the parallelized system it has been noted that this effect is much more severe with the setup described here: Due to the long beam path and the parallel beam geometry, even scattering by only small angles has the consequence that the next mirror is missed and the light is lost. Scattering problems are most severe for materials with particle sizes in the micrometer range and highly anisotropic morphology. One of the worst possible systems in this respect is mordenite, which has a needle-shaped morphology. Thus, it was not possible to investigate the surface acidity of H-MOR, since almost all the light was scattered by the sample and no light carrying information from the zeolite was received at the detector. Zeolite Y and H-ZSM-5, however, could be analyzed without problems, as well as several other samples used for comparison, such as amorphous silica and other types of ZSM-5. The problem is more severe at higher wavenumbers, though, so that in general poor spectra are obtained for the

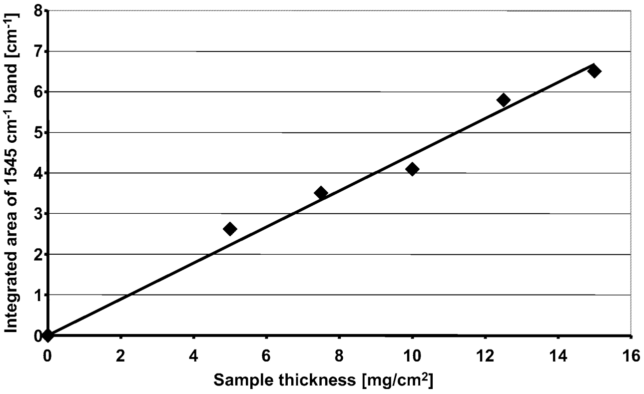

Fig. 2. Correlation between the thickness of sample and the integrated absorbance of the band of Brønsted acid sites at 1545 cm^{-1} (integration limits 1510–1570 cm^{-1}). Samples had been heated at 250 °C before the analysis.

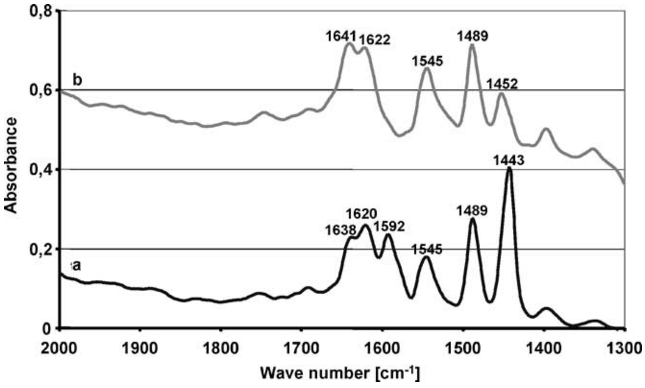

Fig. 3. IR spectrum of sorbed pyridine on the surface of zeolite Y (10 mg/cm^2) before heating (trace a) and after heating at 250 °C for 15 min (trace b) recorded in parallel mode with the FPA detector. The spectra are for the same sample at the same position in the cell.

OH-stretching range. Strong scattering from one sample position does not affect the data quality obtained for the other samples. Only a very minor fraction of the light scattered from one position is collected onto pixels corresponding to other positions, and thus the spectra of other positions are not influenced in any measurable way if a highly scattering sample is present in the cell. Thus, there is no problem in measuring eight different samples in one experiment, and most of the experiments discussed in the following have in fact been performed in this manner. In the following only the results of the measurements with zeolite Y, H-ZSM-5, and silica as nonacidic reference material will be presented in order to illustrate the possibilities offered by the technique.

Sample thickness was found to be an important parameter for this kind of analysis of acid sites. Using the zeolite Y sample the influence of the sample thickness on the spectra has been analyzed in parallel mode (Fig. 2).

As can clearly be seen in Fig. 2, there is the expected linear correlation between thickness of samples and the integrated absorbance of a representative band (in this case the band of Brønsted acid sites at 1545 cm^{-1} after heating of the sample to 250 °C). If samples are thicker than 15 mg/cm^2 scattering is too severe and no reliable analysis is possible any more. The thickness found appropriate for analysis in the parallel mode corresponds roughly to the thicknesses typically used in conventional experiments where most of the studies use a thickness between 5 and 30 mg/cm^2 [29].

Reproducibility of spectra with identical sample thickness was generally high. Although we did not run sufficiently many repeats to calculate a proper standard deviation, integrated intensities of the bands of adsorbed pyridine determined in repeated experiments starting with a new preparation of the sample did not deviate by more than 10% in all cases and typically were below 5%.

With this kind of measurement cell, the strength of the acid sites can be investigated within certain limits as well. This limit is given by the maximum temperature of the cell, which could, however, be raised as stated in the experimental part. By heating of the samples physisorbed pyridine molecules can be removed from the surface, while pyridine species adsorbed on either Brønsted or stronger Lewis acid sites remain adsorbed even after heating at 250 °C. This effect is easily seen in the spectra of pyridine on zeolite Y (Fig. 3).

Before heating both bands of physisorbed pyridine can clearly be identified in the IR spectrum of the sample at 1443 and 1592 cm^{-1} (Fig. 3, trace a). The strong band at 1443 cm^{-1} overlaps completely with the band of Lewis acid sites at 1452 cm^{-1}, which thus cannot be observed.

However, after heating of the sample at 250 °C for 15 min physisorbed pyridine is removed from the surface completely and merely stronger bonded chemisorbed pyridine remains (Fig. 3, trace b). The disappearance of the high intensity band at 1443 cm^{-1} now also allows detection of the band of Lewis acid sites at 1452 cm^{-1}. The IR spectrum shows reproducibly all chemisorbed species on the surface of the zeolite Y samples which have been analyzed various times in different runs.

Completely analogously it was possible to analyze the acidity of the surface of H-ZSM-5. As with the H-Y sample all characteristic bands can be recorded via parallelized measurements (Fig. 4). In the case of the nonacidic amorphous silica sample only physisorbed pyridine can be detected at room temperature. After heating there is no pyridine left on the surface of the sample (Fig. 5).

In order to check the reliability of the method, all samples were also measured in a conventional setup for IR analysis of adsorbed pyridine. In general, the agreement was rather good. Fig. 6 gives a typical comparison of the result of the parallelized measurement and the conventional analysis for the H-ZSM-5 sample.

The IR spectrum of the conventional measurement setup has been recorded with a resolution of 2 cm^{-1}. The IR spectrum of the FPA IR detecting system has been recorded with a resolution of 8 cm^{-1}. Both spectra show all expected characteristic bands. It should be noted, though, that the peak-to-peak noise in the parallelized mode is by about a factor of 10 higher than that in the conventional setup. This, however, is

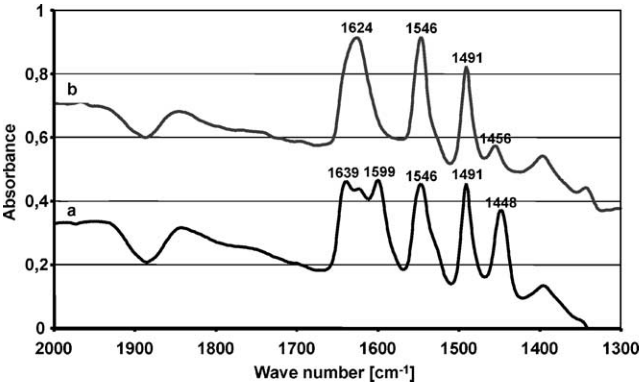

Fig. 4. IR spectrum of sorbed pyridine on the surface of H-ZSM-5 (10 mg/cm^2) before heating (trace a) and after heating at 250 °C for 15 min (trace b) recorded in parallel mode with the FPA detector. The spectra are for the same sample at the same position in the cell.

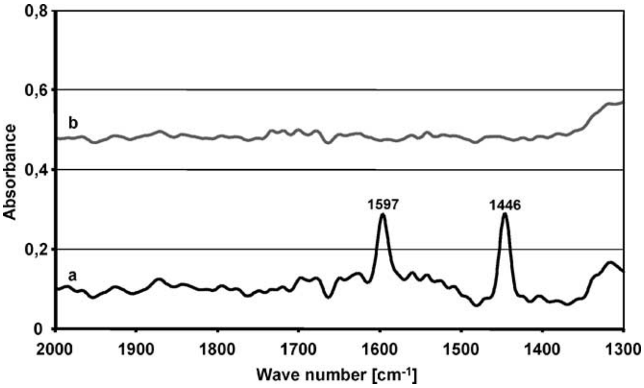

Fig. 5. IR spectrum of sorbed pyridine on the surface of amorphous silica (10 mg/cm^2) before heating (trace a) and after heating at 250 °C for 15 min (trace b) recorded in parallel mode with the FPA detector. The spectra are for the same sample at the same position in the cell.

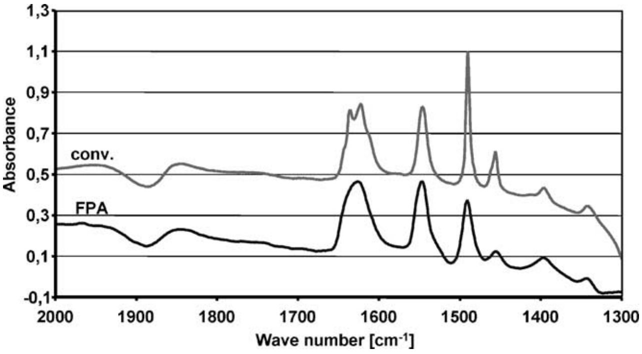

Fig. 6. Comparison of IR spectra that were obtained with a conventional IR spectrometer as well as with the FPA IR detecting system. The IR spectra show sorbed pyridine on the surface of H-ZSM-5. The samples had been heated up to 250 °C for 15 min before measurement.

not a severe limitation for the analysis of acidity using pyridine adsorption, since the S/N ratio is more than sufficient for reliable analysis even with the parallel setup, as demonstrated in the spectra.

Table 2
Concentration of Brønsted acid sites (BA) in zeolite Y and H-ZSM-5

Technique	*c* (BA) in zeolite Y [μmol/cm^3]	*c* (BA) in H-ZSM-5 [μmol/cm^3]
FPA IR detection	1135	747
Conventional IR spectroscopy	1136	765
Chemical analysis/NMR	1885	1244

Comparison of the results of IR spectroscopic measurements (obtained in the parallel cell on one position) with an estimation based on chemical analysis in connection with NMR spectroscopy.

The integral absorbance of the bands for both methods are given in Table 2, together with the concentration of acid sites calculated using the extinction coefficients of Emeis [30] and the concentration of Brønsted acid sites as calculated from the Si/Al ratio and the fraction of framework aluminum atoms as measured by ^{27}Al MAS NMR spectroscopy. The agreement between the parallelized and the conventional setup is acceptable. Also the agreement between the analysis of the concentration of Brønsted acid sites by IR and by chemical analysis/NMR spectroscopy appears satisfactory, especially if one keeps in mind that the extinction coefficients for adsorbed pyridine differ by a factor of 4 in the literature [30–32]. The fact that for both zeolite Y and H-ZSM-5 the concentration determined by IR spectroscopy is only about 60% of the one determined by chemical analysis/NMR spectroscopy supports the notion that the extinction coefficient of Emeis is not fully correct.

A somewhat stronger deviation between parallelized and conventional analysis is observed for the band at 1456 and 1490 cm^{-1}. This deviation is partly caused by the lower resolution of the parallelized setup which leads to a less pronounced central peak. In addition, the fact that the temperature at the sample is not identical for both measurement cells, even if it is nominally the same, may contribute by a slightly different degree of desorption of pyridine from Lewis acid sites. There may thus be a lower amount of pyridine adsorbed on Lewis acid sites in the parallelized setup. Also due to the lower resolution of the IR spectrum of the FPA IR detecting system minor bands like the one at 1635 cm^{-1} are not resolved. Instead of that only the envelope of both maxima can be seen.

The results presented show that the parallelized analysis of solid acidity using pyridine adsorption in combination with IR analysis using a FPA detector is in principle possible. Complications can arise for strongly scattering sample, which cannot be analyzed due to the longer path length of the IR radiation which leads to loss of light scattered by even very low angles. In order to solve or minimize such problems, a complete redesign of the optical path and the analysis cell would be necessary.

The measurement itself takes around 15 minutes, which is short compared to the rest of the procedure. However, even this time could be shortened if the rapid scan procedure developed by Lauterbach and co-workers would be implemented [20,21]. However, this does not seem to be necessary, since heating, cooling, and pumping cycles are the most time-consuming steps. Even in the present state, the method allows the acidity analysis to be faster by a factor of 8, and higher integration to a parallelization degree of 30 seems straightforward, since a reasonable S/N is obtained with even one pixel, provided that scattering from the sample is not too strong. Also extension to a high-temperature cell is easily possible, so that all experiments involving pyridine adsorption on acidic materials can be carried out in parallelized mode with data quality approaching that of conventional analysis. This technique could be especially interesting for laboratories where large numbers of samples must be analyzed in routine mode with respect to their acidity.

4. Conclusions

We have demonstrated the feasibility of parallelized acidity analysis using pyridine adsorption in combination with a spatially resolving IR detector. This provides semiquantitative data comparable to those from a conventional experiment and can thus considerably speed up the lengthy procedure of acidity analysis.

The measurement cell itself is not restricted to the application in parallelized pyridine sorption measurements. In principle, all IR spectroscopic methods for the analysis of surface properties of solids are parallelizable using this cell. Especially interesting applications are in fields where high sample numbers are analyzed and the time needed per sample is rather long. One such field is the determination of surface area and other textural properties which is conventionally done with nitrogen adsorption at liquid nitrogen temperature which is very difficult to parallelize. Possibly, a hydrocarbon adsorption method analyzed by FPA IR spectroscopy could provide almost equivalent information, but on a much shorter time scale. The measurement cell described here could also be used for such experiments.

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References

[1] J.M. Newsam, F. Schüth, Biotechnol. Bioeng. 61 (1999) 203.
[2] B. Jandeleit, D.J. Schaefer, T.S. Powers, H.W. Turner, W.H. Weinberg, Angew. Chem. Int. Ed. 38 (1999) 2495.
[3] S. Senkan, Angew. Chem. Int. Ed. 40 (2001) 312.
[4] D.E. Akporiaye, I.M. Dahl, A. Karlsson, R. Wendelbo, Angew. Chem. Int. Ed. 37 (1998) 609.
[5] J. Klein, C.W. Lehmann, H.-W. Schmidt, W.F. Maier, Angew. Chem. Int. Ed. 37 (1998) 3369.
[6] S. Senkan, K. Krantz, S. Ozturk, V. Zengin, I. Onal, Angew. Chem. Int. Ed. 38 (1999) 2965.
[7] M. Schwickardi, T. Johann, W. Schmidt, O. Busch, F. Schüth, Stud. Surf. Sci. Catal. 143 (2002) 93.
[8] C. Hoffmann, A. Wolf, F. Schüth, Angew. Chem. Int. Ed. 38 (1999) 2800.
[9] C. Hoffmann, H.-W. Schmidt, F. Schüth, J. Catal. 198 (2001) 348.
[10] I. Hahndorf, O. Buyevskaya, M. Langpape, G. Grubert, S. Kolf, E. Guillon, M. Baerns, Chem. Eng. J. 89 (2002) 119.
[11] P. Claus, D. Hönicke, T. Zech, Catal. Today 67 (2001) 319.
[12] T. Johann, A. Brenner, M. Schwickardi, O. Busch, F. Marlow, S. Schunk, F. Schüth, Angew. Chem. Int. Ed. 41 (2002) 2966.
[13] O.M. Busch, C. Hoffmann, T.R.F. Johann, H.-W. Schmidt, W. Strehlau, F. Schüth, J. Am. Chem. Soc. 124 (2002) 13527.
[14] F. Schüth, O. Busch, C. Hoffmann, T. Johann, C. Kiener, D. Demuth, J. Klein, S. Schunk, W. Strehlau, T. Zech, Top. Catal. 21 (2002) 55.
[15] F.C. Moates, M. Somani, M. Annamalai, J.T. Richardson, D. Luss, R.C. Wilson, Ind. Eng. Chem. Res. 34 (1996) 4801.
[16] H. Su, E.S. Yeung, J. Am. Chem. Soc. 122 (2000) 7422.
[17] E. Reddington, A. Sapienza, B. Guraou, R. Viswanathan, S. Sarangapani, E.S. Smotkin, T.E. Mallouk, Science 280 (1998) 1735.
[18] Y. Liu, P. Cong, R.D. Doolen, H.W. Turner, W.H. Weinberg, Catal. Today 61 (2000) 87.
[19] A. Holzwarth, H.-W. Schmidt, W.F. Maier, Angew. Chem. Int. Ed. 37 (1998) 2644.
[20] C.M. Snively, G. Oskarsdottir, J.A. Lauterbach, Angew. Chem. Int. Ed. 40 (2001) 3028.
[21] C.M. Snively, G. Oskarsdottir, J.A. Lauterbach, Catal. Today 67 (2001) 357.
[22] R.J. Hendershot, P.T. Fanson, C.M. Snively, J.A. Lauterbach, Angew. Chem. Int. Ed. 42 (2003) 1152.
[23] O.B. Vistad, D.E. Akporiaye, K.P. Lillerud, J. Phys. Chem. B 105 (2001) 12437.
[24] C.M. Snively, S. Katzenberger, G. Oskarsdottir, J. Lauterbach, Opt. Lett. 24 (1999) 1841.
[25] L. Forni, Catal. Rev. Sci. Eng. 8 (1973) 65.
[26] W.E. Fameth, R.J. Gorte, Chem. Rev. 95 (1995) 615.
[27] E.P. Parry, J. Catal. 2 (1963) 371.
[28] M.R. Basila, T.R. Kantner, K.H. Rhee, J. Phys. Chem. 68 (1964) 3197.
[29] Niemantsverdriet, Spectroscopy in Catalysis, VCH, Weinheim, 1993, p. 200.
[30] C.A. Emeis, J. Catal. 141 (1993) 347.
[31] J. Datka, A.M. Turek, J.M. Jehng, I.E. Wachs, J. Catal. 135 (1992) 186.
[32] T.R. Hughes, H.M. White, J. Phys. Chem. 71 (1967) 2192.