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DOI:
[10.1039/C8CP05001E](https://doi.org/10.1039/C8CP05001E)

Document Version

Accepted author manuscript

[Link to publication record in Manchester Research Explorer](#)

Citation for published version (APA):

Brauer, P., & D'Agostino, C. (2018). Base adsorption mechanism over zeolite catalysts at different Al content probed by the tapered element oscillating microbalance (TEOM). *Physical Chemistry: Chemical Physics*, 20(39), 25357-25364 . <https://doi.org/10.1039/C8CP05001E>

Published in:

Physical Chemistry: Chemical Physics

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**Base adsorption mechanism over zeolite catalysts at different Al content
probed by the tapered element oscillating microbalance (TEOM)**

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Abstract

Acidity of zeolites is a paramount property that determines their behaviour in catalytic and adsorption applications. Various techniques have been established over the years to characterise this property qualitatively and quantitatively, using different indicators able to reveal different insights. In this work, for the first time we have used the tapered element oscillating microbalance (TEOM) to study quantitative aspects of internal and external zeolite acidity by measuring sorption dynamics of pyridine and collidine over HZSM5 zeolites with different silica-to-alumina ratio (SAR). The method is able to easily quantify, with a rapid and robust calibration procedure, maximum, physisorbed and chemisorbed uptake of probe molecules. The results show that the uptake of both pyridine and collidine measured by the TEOM increases with decreasing SAR, that is, increase in Al content, consistently with the increase in acid site density at increasing Al content. Most importantly, by providing a robust and easy-to-interpret set of data, the experimental protocol reveals new fundamental insights into the adsorption mechanism as a function of the Al content, showing that at high Al content chemisorption is the major adsorption mechanism, whereas at low Al content physisorption becomes the dominant mechanism.

Key words: tapered element oscillating microbalance, zeolites, acidity, adsorption

Introduction

Zeolites are an important class of materials widely used in many applications, including as catalysts, molecular sieves and adsorption media.^{1, 2} One important feature of zeolites is that of surface acidity, which affects catalytic activity as well as adsorption kinetics of these materials.^{3, 4} Acidic properties of zeolites may be quantified by measuring the uptake of suitable probe molecules, usually base molecules such as ammonia or pyridine, using a variety of techniques.⁵ Established methods include infrared (IR) spectroscopy^{6, 7} and temperature-programmed desorption (TPD).⁸ IR is very useful to qualitatively study surface acidity, being able to distinguish between different types of acid sites, most notably Lewis and Brønsted sites; molar extinction coefficients must be determined for each type of acid sites if IR spectra are to be quantified. A recent work on pyridine adsorption over HZSM5 zeolites has demonstrated that by combining IR measurements with elemental analysis and some suitable sample treatment it is possible to a certain extent obtain quantitative information on surface acidity.⁹

For a more quantitative analysis, TPD is perhaps the most widely used technique, which consists in recording a desorption profile of a probe species, such as ammonia or pyridine, as a function of temperature. The TPD profile may be recorded either by a mass spectrometer (MS) or gas chromatography (GC). However, in order to have a proper quantification in terms of uptake of probe species per unit mass of catalyst, a suitable calibration of the TPD profile is required, which may result in lengthy and non-trivial experimental procedures.¹⁰

An alternative valid approach for tackling such an issue is represented by the use of the tapered element oscillating microbalance (TEOM).¹¹ Due to its high mass and temporal resolution, this technique is a powerful tool to study adsorption and desorption processes at equilibrium but also in terms of dynamic processes, before equilibrium is reached. The main principles of the TEOM is that of probing uptake of adsorbing species by measuring changes in oscillation frequency of the tapered element, essentially an oscillating adsorption chamber. The main advantage of using the TEOM for quantifying adsorption uptake is that only the spring constant K_0 must be calibrated, which can be done in a very rapid and straightforward manner.

Initially, the TEOM was developed to measure the concentration of dust particles in gases¹² and is still widely used for this purpose.¹³ However, its characteristics such as high mass and temporal resolution make it especially suitable for investigating phenomena in catalysis. Hence, it has been used to elucidate mass changes during reduction treatments¹⁴ as well as in studies of coke formation on catalysts.¹⁵⁻¹⁷ The TEOM has also been used to measure

equilibrium adsorption isotherms^{18, 19} and adsorption/desorption kinetics.²⁰⁻²³ There has also been research effort to employ the TEOM to obtain an insight into the combined effects of adsorption, diffusion, reaction and coking.²⁴

Zhu et al.¹⁹ used the TEOM to investigate the shape selectivity of propane and propene adsorption on zeolite DD3R and reported a much lower uptake for the alkene compared to the alkane. This was attributed to the different critical-molecular diameter. Rebo et al.²³ investigated the adsorption of toluene, *p*-xylene and *o*-xylene in HZSM5 at various temperatures (303-473 K) and partial pressures (0.2-10 kPa) using the TEOM. For each experimental condition the mass uptake order was *p*-xylene > toluene > *o*-xylene. The kinetic diameter of *o*-xylene (6.8 Å) is larger than the one for *p*-xylene and toluene, which both exhibit a kinetic diameter of 5.9 Å. (24) Thus, *o*-xylene is expected to have the lowest uptake. After converting the uptake from mass ($\text{g}_{\text{ads}} \text{g}_{\text{zeolite}}^{-1}$) to moles ($\text{mol}_{\text{ads}} \text{g}_{\text{zeolite}}^{-1}$), the values for *p*-xylene and toluene were very comparable indicating the importance to distinguish between mass and mole uptake of probe molecules.

It is clear that the use of the TEOM to study adsorption and desorption processes over solids has mainly focused on hydrocarbons adsorbed in various catalysts and porous materials. However, to the best of our knowledge, the method has not been used yet to elucidate and quantify acidic properties of zeolites, both in terms of sorption dynamics or uptake of base probe molecules.

In this work we investigate the use of TEOM as an additional tool to characterise internal and external acidic properties of zeolites using pyridine and collidine as probe species. The use of pyridine to probe internal acidity was preferred to that of ammonia, the latter being a much more hazardous substance, more difficult to handle and which may also create issues related to corrosion of piping of the experimental set-up. In addition, the molecular structures of pyridine and collidine are very similar, with the main difference being the size, which is what we are interested in when probing access to the pore space of the zeolites. Hence, the uptake of pyridine and collidine over HZSM5 zeolite samples with different silica-to-alumina (SAR) ratio was chosen as a model system to study both internal and external acidity of the zeolite samples, respectively, probing maximum, physisorbed and chemisorbed uptake, hence validating the use of this experimental approach as a tool to investigate zeolite acidity and give new insights into the adsorption mechanisms over these materials.

Experimental

Materials and chemicals

Pyridine (99%) was obtained from Alfa Aesar. Collidine (99%) was obtained from Sigma Aldrich. All chemicals were used as supplied. Several ZSM5 samples with various SAR ($\text{SiO}_2/\text{Al}_2\text{O}_3$) values of 23, 30, 50, 80 and 300 were purchased from Alfa Aesar in the NH_4^+ form. Zeolite samples were calcined in a furnace with synthetic air ($100 \text{ cm}^3 \text{ min}^{-1}$, Air Liquide) at 773 K for 4 h to convert from the NH_4^+ to the H^+ form, termed HZSM5. Heating and cooling were carried out at 5 K min^{-1} . Samples were named according to their SAR, as supplied by Alfa Aesar, and denoted as HZSM5 (SAR). The surface area of these samples is in the range $400 - 425 \text{ m}^2 \text{ g}^{-1}$, as stated by Alfa Aesar. Additionally, Sand (SiO_2 , 50 - 70 mesh particle size) was obtained from Sigma-Aldrich.

TEOM set-up and experiments

The TEOM set-up used in this work to carry out pyridine and collidine sorption experiments is schematically shown in Figure 1. Experiments were performed using a TEOM Rupprecht and Patashnick, 1500 Pulse Mass Analyser (PMA) Model. The TEOM was situated on anti-vibration pads and equipped with a pressure gauge at the inlet and a thermocouple (K-type, $\pm 0.75\%$) monitoring the sample temperature at the furnace wall. Helium was supplied from a gas cylinder and directed through a molecular sieve moisture trap (Alltech Hydro-Purge II) to mass flow controllers (Tylan General FC-260 and Unit Instruments UFC-1100N, accuracy $\pm 1\%$). Pressure gauges were placed at each mass flow controller outlet together with both non-return valves and pressure release valves, rated to 5 bar, to prevent back flow and as a safety measure. A stainless-steel saturator containing liquid pyridine or collidine was held at 288 K in a thermostatic bath (Julabo F32-HC).

The helium purge flow around the tapered element was used to prevent the effluent stream from re-entering the packed sample bed. The automated four-port valve allowed for feed switching between dry helium (termed pre-treat stream) and saturator flow (termed carrier stream), that is, helium containing pyridine or collidine vapour. Before adsorption experiments were started, the needle valves on each vent line were adjusted such that the pressure in each line was identical to prevent a change in gas pressure and density within the tapered element when the feed was switched. Data acquisition and control of the flows, temperatures and valves was performed using LabVIEW software v8.6.

For pyridine and collidine sorption experiments HZSM5 powder ($20 \pm 0.5 \text{ mg}$) was placed between quartz wool and held in place by a stainless-steel cap containing holes covering the

end of the element. HZSM5 samples were activated in flowing helium (40 ml min^{-1} STP) by heating to 673 K at 3 K min^{-1} , holding for 1 h and then cooling to 423 K at 3 K min^{-1} . The tapered element was left in flowing helium for at least 1 h after activation to establish a flat baseline. The feed was then changed to the saturator (carrier stream) containing pyridine or collidine and the mass change was recorded with a gate time of 0.8 s , that is, a frequency measurement was taken every 0.8 s . After maximum adsorption was reached, indicated by reaching a constant frequency, the feed was switched back to helium (pre-treat stream) and the packed sample with adsorbed probe molecules was left for 2 h to obtain the amount of chemisorbed probe molecules, pyridine or collidine. A helium purge flow (10 ml min^{-1} STP) was used for the entire duration of each experiment.

Figure 1. Schematic of TEOM set-up for pyridine and collidine sorption measurements with liquid saturator. MFC = mass flow controller, TC = thermocouple, P = pressure gauge.

Methodology

By measuring the variation in the resonance frequency of the tapered element the TEOM probes changes in sample mass. The spring constant K_0 of the tapered element, which is needed for quantification, is easily calibrated according to:

$$\Delta M_{\text{cap}} = K_0 \left(\frac{1}{f_{\text{cap}}^2} - \frac{1}{f_0^2} \right) \quad (1)$$

In order to do this, TEOM experiments were carried out to measure the oscillation frequency of the tapered element with the cap (f_{cap}) and without the cap (f_0); thus, knowing the mass of the cap, ΔM_{cap} , which was measured as 0.223 g, it is possible to calculate the calibration constant K_0 . The frequency measurements were conducted between temperatures of 323 and 573 K to investigate if any temperature dependence of the spring constant was present. The observed temperature variation for K_0 was very small, reflected in the standard deviation of the calculated mean value for the spring constant in the studied temperature range, $2.314 \pm 0.001 \text{ N m}^{-1}$.

Once a catalyst sample is packed in the tapered element, void space will be present between the catalyst particles. During a TEOM experiment probe molecules are adsorbing and desorbing from the catalyst surface in this void space. Therefore, the density of the so-called “dead volume” might change due to different amounts of probe molecules being present in the gas phase. Depending on the amplitude of this change in gas density the overall observed mass change ΔM might be affected. In particular:

$$\Delta M = \Delta M_a + \Delta M_g = K_0 \left(\frac{1}{f_1^2} - \frac{1}{f_0^2} \right) \quad (2)$$

where ΔM_a is the mass change due to adsorption on the catalyst surface and ΔM_g is the mass change due to changes in gas density. Therefore, to obtain the mass change due to the adsorption on the catalyst surface (ΔM_a) only it is normally necessary to subtract results measured on a material with negligible adsorption, such as quartz, from the results measured with the catalyst of interest both acquired at identical experimental conditions.

In this regard, to assess the effect of density change of the dead volume in the tapered element pyridine sorption experiments were carried out at 423 K with quartz particles (Sand) to minimise adsorption on the surface of the packed material. For this experiment, the change

in frequency was recorded after switching from the pre-treat stream (helium) to the carrier stream (pyridine vapour), that is, helium gas that passed through the saturator containing liquid pyridine at 288 K. The change in mass recorded after switching to the carrier stream was within the bandwidth of the experimental noise ($\Delta M = 1 \mu\text{g}$), which can be regarded as the lower limit for mass changes that can be reliably probed by the used TEOM set-up. Therefore, the effect of the density change of the dead volume due to pyridine was negligible. Collidine has a lower vapour pressure than pyridine at 298 K the values being 1.99 mmHg²⁵ and 20.8 mmHg,²⁶ respectively. Furthermore, collidine has a lower density than pyridine at 293 K with 0.913 compared to 0.983 g cm³, respectively.^{27, 28} Therefore, the mass change of the dead volume caused by collidine is expected to be even smaller than the one measured for pyridine. In summary, for pyridine and collidine TEOM experiments the mass adsorbed on the HZSM5 samples was significantly greater than the mass change in the dead volume, that is, the space between the catalyst particles. The correction of the acquired catalyst data by the quartz data to obtain the mass change that is only due to adsorption on the catalyst surface was therefore not required in this work.

The frequency of data point acquisition of the TEOM, termed gate time, can be set to values between 0.1 and 0.8 seconds. Shorter gate times will result in a higher resolution of the sorption data but will also give a higher normalised standard deviation (NSD), or noise level. The adsorption and desorption dynamics investigated in this work were rather slow and a short gate time was therefore not necessary. Thus, to acquire sorption data with a low NSD, that is low noise level, a gate time of 0.8 s was selected for all TEOM experiments conducted in this work unless stated otherwise.

Results and discussion

Pyridine TEOM uptake studies

The TEOM set-up was used in this work to firstly measure the maximum pyridine uptake at 423 K, which includes both physisorbed and chemisorbed species, while the carrier stream, with a pyridine vapour pressure of 0.016 bar, was flowing through the packed bed of the tapered element containing the zeolite sample. Figure 2 depicts the pyridine sorption profiles measured by the instrument at this temperature. It can be seen from the figure as initially the pyridine uptake onto the zeolite samples steeply rises to a maximum value and remains constant after saturation has been reached. After a time of 0.5 h the flow is switched from the carrier stream containing pyridine to a stream of dry helium, which desorbs weakly adsorbed pyridine molecules. After a rapid decrease, the profile becomes flat and the pyridine uptake

reaches a new steady value after a time of approximately 2 h, which corresponds to the amount of chemisorbed pyridine, that is, the amount of pyridine left after the dry helium purge of the zeolite sample saturated with pyridine. Hence, in a single experiment it is possible to quantify and easily visualise maximum, chemisorbed and physisorbed uptake in a rather straightforward fashion and without the need of assumptions that may affect quantification.

In terms of effect of SAR of the zeolite onto the pyridine uptake, the amount of both maximum and chemisorbed pyridine increases with decreasing SAR, that is, increasing total Al content, with the HZSM5 (23) and HZSM5 (300) samples showing the highest and lowest uptake, respectively. This is consistent with previous findings reporting that an increase in Al content leads to an increase in overall acidity of the zeolite.⁹ The pyridine uptake is comparable for HZSM5 with SAR values of 50 and 80. It is noted that the maximum pyridine uptake of HZSM5 (80) is slightly higher than the maximum pyridine uptake of HZSM5 (50) although the difference is not large.

Figure 2. Pyridine sorption profiles measured by the TEOM at 423 K for HZSM5 with varying SAR (indicated in the plot). The uptake (y-scale) is given in gram of pyridine per gram of catalyst (HZSM5 powder). The time $t = 0$ was selected for each plot so that the change in mass starts at the same point on each graph.

The maximum and chemisorbed pyridine uptake were converted to moles using the molecular weight of pyridine, 79.1 mol g^{-1} , and are plotted against the total Al content of the investigated HZSM5 samples in Figure 3 (left). Both types of uptake show almost linear trends with increasing total Al content. The maximum pyridine uptake of HZSM5 (50) and HZSM5 (80) are similar and within the experimental uncertainty. To further investigate the

relationship between the maximum number ($n_{\max}$) and chemisorbed number (n_{chem}) of pyridine molecules the ratio between the two was calculated as follows:

$$\text{ratio}(\max/\text{chem}) = \frac{n_{\max}}{n_{\text{chem}}} \quad (3)$$

Interestingly, it can be observed in Figure 3 (right) that $\text{ratio}(\max/\text{chem})$ decreases with increasing total Al content. However, the $\text{ratio}(\max/\text{chem})$ values become rather similar for HZSM5 with SAR values between 23 and 80, in particular compared to the significantly higher value for the SAR of 300. This suggests that HZSM5 (300) exhibits the highest and HZSM5 (23) the lowest fraction of weakly adsorbed pyridine molecules that are not able to be retained from the acid sites once the TEOM set-up is switched from the carrier (pyridine vapour) to the pre-treat (helium) stream. Hence, at higher Al content a higher proportion of adsorption sites are chemisorption sites, whereas at low Al content physisorption is the dominant adsorption mechanism.

Figure 3. Uptake results (in μmol per gram of catalyst) measured by the TEOM for pyridine adsorbed in HZSM5 with varying SAR (300, 80, 50, 30 and 23 from left to right) at 423 K: **(left)** maximum pyridine uptake during carrier stream (pyridine vapour) and amount of chemisorbed pyridine after 2 h in flowing pre-treat stream (helium). Error bars for the uptake (y-scale) were calculated from the standard deviation of four separate TEOM experiments; **(right)** values for $\text{ratio}(\max/\text{chem})$ defined in Equation (3) for pyridine. Error bars (y-scale) were calculated from the standard deviation of the single values.

Collidine TEOM uptake studies

The probe molecule combination pyridine/collidine has been frequently used to study internal and external acidity in zeolites by means of IR spectroscopy.^{29, 30} Whilst pyridine with a kinetic diameter of 5.7 Å is expected to access both the internal and external surface, collidine with a kinetic diameter of 7.4 Å is expected to access the external surface only.

Using techniques such as IR spectroscopy, the quantification of the fraction of internal and external acid sites, and thus the number of probe molecules adsorbed, requires the knowledge of molar extinction coefficients, which are often not available. Using the TEOM approach, and its easy calibration procedure previously discussed, with the pyridine/collidine combination, the quantification of the total uptake on the internal and external surface of the zeolites, which is important in applications such as adsorptive separation,³¹ becomes rather straightforward.

Figure 4 depicts the collidine sorption profiles measured by the TEOM at 423 K. It can be observed that the maximum and chemisorbed amount of collidine in HZSM5 is significantly less than for pyridine Figure 2. Thus, even though collidine is a stronger base than pyridine, indicated by the proton affinity values of 975 and 930 kJ mol⁻¹, respectively, which would give a higher number of adsorbed collidine molecules, the much lower uptake suggests that collidine is not able to enter the HZSM5 pore network. This is expected based on the kinetic diameter of collidine (7.4 Å) compared to the size of the HZSM5 pore network (sinusoidal channels: 5.3 Å × 5.6 Å, straight channels: 5.5 Å × 5.1 Å).³² Therefore, collidine will interact only with acid sites located on the external HZSM5 crystal surface or situated at the entrances to the pore network.

Figure 4. Collidine sorption profiles measured by the TEOM at 423 K for HZSM5 with varying SAR (indicated in the plot). The uptake (y-scale) is given in gram of collidine per gram of catalyst (HZSM5 powder). The time $t = 0$ was selected for each plot so that the change in mass starts at the same point on each graph.

The maximum and chemisorbed collidine uptake on HZSM5 zeolites with varying SAR converted to moles using the molecular weight of collidine, 121.2 g mol⁻¹, are shown in

Figure 5 (left). The ratio of the two, $\text{ratio}(\text{max}/\text{chem})$ as defined in Equation (3), is depicted in Figure 5 (right). It can be observed in Figure 5 (left) that the number of maximum adsorbed collidine molecules exhibits the highest values for HZSM5 with SAR values of 50 and 80. This agrees with previous findings reported in the literature that reached the same conclusions using IR techniques.⁹ As collidine adsorbs mostly on the external surface of the zeolite, it is likely that the amount of exposed surface area will affect significantly its uptake. Indeed, it was observed that the collidine uptake can be correlated with the external surface area measured by argon adsorption (see Supporting Information). As for chemisorption, the number of chemisorbed collidine molecules in HZSM5 increases with increasing total Al content, which is qualitatively comparable to the trend observed for the number of chemisorbed pyridine molecules depicted in Figure 3 (left). This can be explained by the increase in amounts of external Brønsted acid sites⁹ that is suggested to significantly contribute to the total number of chemisorbed collidine molecules at higher total Al content.

Figure 5. Uptake results (in μmol per gram of catalyst) measured by the TEOM for collidine adsorbed in HZSM5 with varying SAR (300, 80, 50, 30 and 23 from left to right) at 423 K: **(left)** maximum collidine uptake during carrier stream (collidine vapour) and amount of chemisorbed collidine after 2 h in flowing pre-treat stream (helium). Error bars for the uptake (y-scale) were estimated within 10%; **(right)** values for $\text{ratio}(\text{max}/\text{chem})$ defined in Equation (3) for collidine. Error bars (y-scale) were calculated from the standard deviation of the single values.

From Figure 5 (right) it is possible to observe that $\text{ratio}(\text{max}/\text{chem})$ for collidine decreases with increasing total Al content, thus indicating a higher fraction of collidine adsorption sites able to retain the maximum number of adsorbed collidine molecules at higher total Al content. The decrease of $\text{ratio}(\text{max}/\text{chem})$ was already observed for pyridine, as shown in Figure 3 (right), therefore suggesting that at higher Al content most of the external adsorption sites are chemisorption sites, whereas at low Al content physisorption is more significant. It is

likely that the concentration of Al associated with Brønsted acid sites is primarily affecting the fraction of strong adsorption sites as the number of total and external Brønsted Al was seen to increase with increasing total Al concentration.⁹ Furthermore, it was previously suggested that the concentration of external Brønsted Al may affect the strength of external terminal silanol sites,⁷ which are therefore likely to contribute to the decreasing trend of ratio(max/chem) with increasing total Al concentration.

Comparative TEOM analysis of pyridine vs collidine

It is now of interest to compare in more depth the TEOM results for pyridine and collidine over HZSM5 samples with varying SAR. In order to carry out a direct comparison between the two probe species, the change in mass measured by the TEOM was converted to moles. The sorption profiles in terms of molar uptake for both pyridine and collidine are shown in Figure 6. The y-scale (uptake in μmol per gram of catalyst) of both plots differs by an order of magnitude and it can be observed that the total and chemisorbed pyridine uptake is significantly higher than for collidine regardless of SAR. It is noted that the absolute uptake values reported in Figure 6 compare very well with those reported in the literature for similar systems,^{33, 34} which further validates the quantitative data reported in this work. For example, Losch et al.³⁴ have reported total acid site density values for various HZSM5 samples that range between approximately 300 and 1500 $\mu\text{mol g}^{-1}$, which is exactly the same range observed in this study with pyridine.

Figure 6. TEOM sorption profiles of (left) pyridine and (right) collidine on HZSM5 zeolites with varying SAR (indicated in the plots) at 423 K. The y-scales differ by an order of magnitude.

From the plots in Figure 6 it is also possible to extract data on the kinetics of uptake by taking the initial slope of the TEOM profile. For the case of pyridine, values of 313, 105, 104, 115 and 115 $\mu\text{mol g}^{-1} \text{min}^{-1}$ were obtained for SAR values of 23, 30, 50, 80 and 300, respectively. This indicates that the rate of uptake of the most acidic sample, SAR of 23, is much greater compared to the other samples and suggests that to some extent acidity affects not only the final uptake value but also the rate at which probe species are adsorbed. It is noted that some studies seem to indicate that zeolites with lower SAR values have higher heat of adsorption, which could be linked to the higher rate of uptake reported here, although it has to be said that such studies have not been thoroughly conclusive.³⁵⁻³⁹ For the collidine samples accurate values of the initial slope could not be obtained because of the much noisier data due to much lower uptakes.

To compare the maximum amount of pyridine and collidine molecules adsorbed on HZSM5 the following ratio is defined:

$$\text{ratio}_{\text{max}} = \frac{n_{\text{pyridine,max}}}{n_{\text{collidine,max}}} \quad (4)$$

In Equation (4) $n_{\text{pyridine,max}}$ and $n_{\text{collidine,max}}$ are the maximum number of pyridine and collidine molecules adsorbed, respectively. Similarly, the same ratio can be defined for the chemisorbed species:

$$\text{ratio}_{\text{chem}} = \frac{n_{\text{pyridine,chem}}}{n_{\text{collidine,chem}}} \quad (5)$$

where $n_{\text{pyridine,chem}}$ and $n_{\text{collidine,chem}}$ are the chemisorbed number of pyridine and collidine molecules adsorbed, respectively. The change of $\text{ratio}_{\text{max}}$ and $\text{ratio}_{\text{chem}}$ with the total Al content in HZSM5 is depicted in Figure 7. It can be seen that both ratios increase with increasing total Al content indicating that significantly more pyridine molecules are interacting with acid sites than collidine as the SAR decreases, that is, the Al content increases. A steep increase is observed for $\text{ratio}_{\text{chem}}$ between SAR values of 300 and 50 followed by a less strong dependence on the total Al content for SAR values between 50 and 23. This indicates a more pronounced increase in external adsorption sites relative to the increase in total adsorption sites for SAR values of 23 and 30, which is likely due to the significantly higher number of external Brønsted acid sites for those samples.

Figure 7. Comparison of pyridine and collidine TEOM results as ratio for number of pyridine molecules relative to number of collidine molecules for maximum amount, **ratio_{max}**, Equation (4), and chemisorbed amount, **ratio_{chem}**, Equation (5).

From Figure 7 it can also be observed that for the SAR of 300 the **ratio_{max}** is significantly greater than the **ratio_{chem}**, indicating that for this sample a larger number of weaker (physisorption) acid sites that are located inside the pore network, relative to the other SAR values.

Conclusions

In this work we have used the tapered oscillating microbalance (TEOM) technique to study quantitative aspects of zeolite acidity by probing the uptake of pyridine and collidine over a range of HZSM5 zeolites with different silica-to-alumina ratio (SAR) values. It is shown that the technique can easily quantify maximum, physisorbed and chemisorbed uptake of probe molecules (both on the internal and external surface) through a simple and rapid calibration procedure. The results reveal that the uptake measured by the TEOM of both pyridine and collidine increases with decreasing SAR, that is, increase in Al content, which is consistent with the increase in acid site density at increasing Al content. In addition, we find that at high Al content most of the adsorption sites are chemisorption sites, whereas for low Al content physisorption becomes more significant; hence, the technique is able to reveal that at high Al content chemisorption is the major adsorption mechanism, whereas at low Al content physisorption becomes the dominant mechanism, which gives new fundamental insights into how the Al content affects the adsorption mechanism in these materials.

Acknowledgements

We would like to thank Prof. Lynn Gladden for the support and for providing the facilities to carry out this work. We also acknowledge Dr Andy York from Johnson Matthey.

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