

Studying the uptake of aniline vapor by active alumina through in-line monitoring a differential adsorption bed with near-infrared diffuse reflectance spectroscopy

Chen-Bo Cai · Qing-Juan Han · Li-Juan Tang · Lu Xu · Jian-Hui Jiang · Hai-Long Wu · Ru-Qin Yu

Received: 22 February 2008 / Revised: 29 September 2008 / Accepted: 27 October 2008 / Published online: 6 November 2008
© Springer Science+Business Media, LLC 2008

Abstract Through non-invasive monitoring the uptake of aniline vapor by active alumina in a differential adsorption bed (DAB) with near-infrared diffuse reflectance spectroscopy (NIR-DRS), we have studied several features of the adsorption, including isotherm, kinetics and the chemical state of aniline molecules in aniline-alumina system. What is perhaps more important, since the information above is obtained synchronously, the proposed methodology could provide information about the type of adsorption (chemical or physical adsorption), the change of chemical state of aniline in the system during the adsorption process, whether the chemical adsorption and physical adsorption took place simultaneously, the rate of the chemical and physical adsorption, and so on.

Keywords Adsorption · Differential adsorption bed · Near-infrared spectroscopy · In-line process analytical chemistry · Partial least squares model · Isotherm · Kinetics · Aniline · Alumina

1 Introduction

Traditionally, there have been many experimental methods to study the uptake of gas adsorbate on solid adsorbent. In physical chemistry, there are static methods and dynamic

methods for studying adsorption equilibrium, while infrared spectroscopy has become a powerful and normal tool to detect the interaction between the adsorbate and adsorbent. In chemical engineering, pulse chromatography, fixed-bed breakthrough, closed-loop recycle and gravimetric measurement have been used to obtain thermodynamic and kinetic data for optimal design and operation of adsorption units (Mayfield and Do 1991). But each method above has its own deficiencies: for example, static method is time-consuming and needs high vacuum; gravimetric method is not appropriate in a gas flow (common situation in practical adsorption process in chemical industry), and complicated mathematical treatment and unreasonable assumptions of mass transfer may make the result of pulse chromatography, fixed-bed breakthrough and closed-loop recycle methods unreliable. Several new experimental methods, such as Frequency Response Technique (FRT) (Yasuda and Matsumoto 1989; Sun et al. 1994), Wicke-Kallenbach Permeation Method (WKM) (Graaf et al. 1998; Xomeritakis et al. 2005), and Isotope Exchange Technique (IET) (Rynders et al. 1997; Mohr et al. 1999; Cao et al. 2000) have been developed during the last two decades which can be potentially advantageous over the traditional ones. Nevertheless, new inconvenience appears in each method as original shortages have been overcome. For example, in FRT the adsorption process takes place in a nonisothermal environment and its data analysis is also dependent upon unreliable models of mass transfer; WKM avoids the complications of data analysis as well as the nonisothermal problem under certain conditions, but requires a specially formed and representative pellet of the adsorbent that is usually very difficult to be obtained; IET was reported to satisfactorily solve almost all difficulties mentioned before, while requiring a supply of isotopes for the adsorbate gas and a continuous on-line analytical device (such as a quadrupole mass spectrometer) for quanti-

C.-B. Cai · Q.-J. Han · L.-J. Tang · L. Xu · J.-H. Jiang · H.-L. Wu · R.-Q. Yu (✉)

State Key Laboratory of Chemo/Biosensing and Chemometrics, College of Chemistry and Chemical Engineering, Hunan University, Changsha 410082, People's Republic of China
e-mail: rquyu@hnu.cn

C.-B. Cai
e-mail: ccp66516@163.com

tative measurement of trace isotope concentrations (Sircar 2007). Above all, all these methods mentioned share one kind of incapacity that they cannot simultaneously provide information about thermodynamics, kinetics and the chemical state of the adsorbate molecules on the surface of the adsorbent, while this simultaneous information might largely improve our understanding of an adsorption process.

Process analytical chemistry (PAC) may help us to acquire all information mentioned above simultaneously. However, gas-solid adsorption systems include at least two phases, i.e., the adsorbent solid and the adsorbate gas, making most common PAC techniques like chromatography or flow injection analysis impossible for in-line monitoring. In addition, these methods cannot provide the information about the chemical state of the adsorbate. As for spectroscopic methods, near-infrared spectroscopy (NIR) seems to dominate spectroscopic work for real-time and process analysis (Workman et al. 2003), because: it is a non-invasive or non-destructive; solid sample can be directly measured without pretreatment if an appropriate device is used; optical fiber makes remote monitoring or control possible; quantitative and simultaneous measurement of all components; rapid response (usually less than 10 seconds); low analytical cost; and the possibility to investigate interaction between adsorbent and adsorbate molecules (Blanco and Villarroya 2002).

Obviously, in order to investigate the chemical state of the adsorbate on the adsorbent, it is required to probe the solid adsorbent containing the adsorbate by NIR-DRS rather than probe the vapor of adsorbate by NIR diffuse transmission spectroscopy. In addition, two advantages that one could get from the idea are: 1) adsorbate vapor could be concentrated by the adsorbent so that the adsorbate vapor with low concentration could be detected with NIR-DRS, too;

2) with the NIR-DRS we could directly measure the concentration of the adsorbate adsorbed by the adsorbent, and consequently avoid error associated with measuring volume, pressure and the like. To our knowledge, it seems that such an approach differs from all other related reports until now (Ferreira et al. 2005; Zhang and Lee 1997).

2 Experimental

2.1 Materials

Active alumina (average pore diameter: 3–5 nm; produced by Sinopharm Chemical Reagent, Shanghai, China) was selected as the adsorbent, and aniline (analytical reagent, produced by the same company) as the adsorbate.

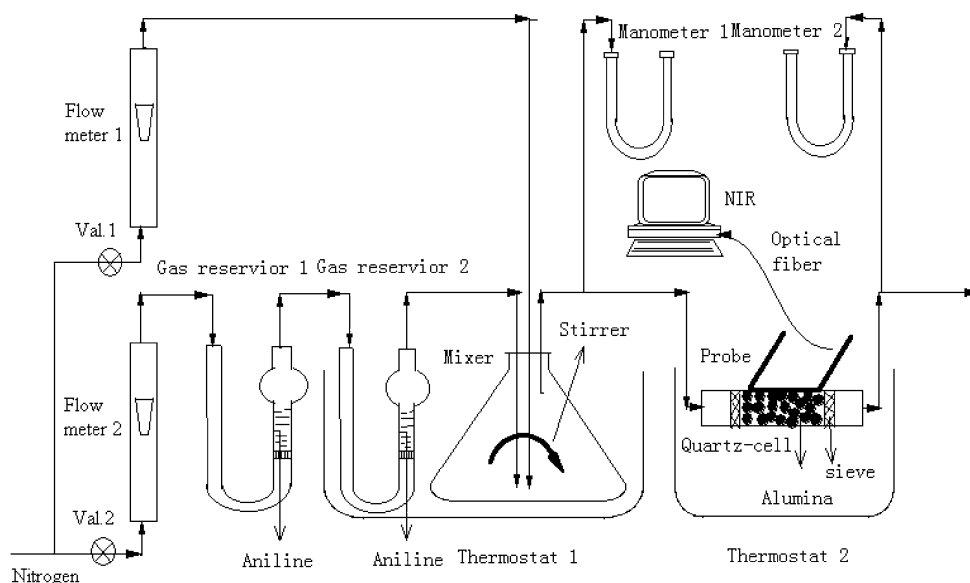
2.2 Near-infrared instrument and measurement

All NIR measurements were implemented with an FT-IR/NIR spectrometer (Nexus 870, Nicolet) furnished with an indium gallium arsenide (InGaAs) detector. The optical fiber probe (Smart Near-IR FiberPort Accessory) was used for monitoring. All spectra were recorded under the same conditions, i.e., resolution: 8 cm^{-1} ; number of scans: 16; range of scans: $4000\text{--}10000\text{ cm}^{-1}$. All the collected spectra are difference spectra, namely, subtracting their reference (i.e. the alumina) spectra from sample spectra to obtain “pure” spectral effect of the aniline.

2.3 Experimental setup

Scheme 1 shows the experimental setup. Pure nitrogen gas was introduced through valves 1 and 2. Part of the N_2 flowed

Scheme 1 Experimental setup



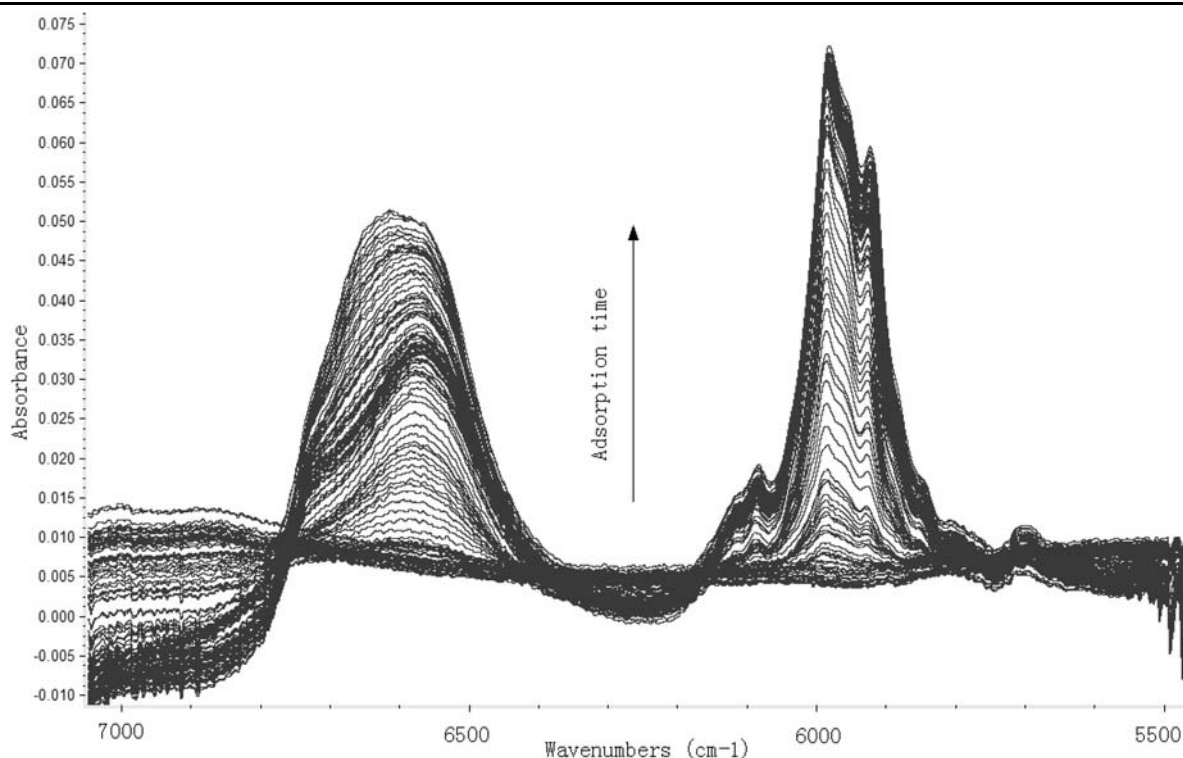


Fig. 1 Raw NIR-DRS during alumina-aniline adsorption process. $T = 303.15$ K; $P/P_0 = 1.00$; $F_0 = 400$ ml/min

through gas reservoirs 1 and 2, which contained liquid aniline. After coming out of the gas reservoir 2, the N_2 was already saturated by aniline vapor, and then mixed with another part of N_2 in a mixer that had a stirrer to improve blending. Later the mixture gas was ushered into a rectangular quartz-cell (40 mm in length, 10 mm in width and 2 mm in thickness), where the gas penetrated through alumina and was adsorbed by it. At the same time, the NIR-DRS of the alumina containing aniline were continuously recorded by the NIR spectrometer via the optical fiber probe.

In the experimental setup above, the temperature of the system was controlled by two thermostats (in the second one, only air is circulated in order to avoid affecting NIR-DRS detection). The concentration of aniline in the gas and the volume flow rate of influent gas (F_0) can be altered by two valves and measured through two flow meters and two manometers. The concentration of aniline in the gas is usually represented as the ratio of the partial pressure (P) to the saturated vapor pressure (P_0) of aniline at the same temperature, i.e., P/P_0 . Besides the amount of aniline in alumina and temperature, the NIR-DRS of alumina are still influenced by three other factors, i.e., the granularity, the thickness and the packing density of alumina. The first factor can be compensated by sampling the alumina with the same sieve; the second one is not a problem when all experiments are performed in the same rectangular quartz-cell; if the same amount of alumina is compressed into the same

length in the same rectangular quartz-cell, the difference in packing density between two experiments disappears (of course, the alumina can neither be compressed so tightly that the gas penetrates it difficultly, nor so loosely that part of the alumina does not contact the gas at all). For all experiments in the present study, the same rectangular quartz-cell of 2 mm in thickness was used; the granularity of alumina was 100–120 meshes; and 0.2000 g of alumina was compressed into 10 mm in the quartz-cell.

Figure 1 shows spectra within 5500–7000 cm^{-1} resulted from monitoring uptake of aniline by alumina with experimental setup and procedure described above. Here, NIR-DRS were recorded from the beginning of adsorption process to the equilibrium state. From the figure we can clearly see that the aniline was adsorbed by the alumina gradually as the process went on.

3 Results and discussion

3.1 Chemometrics model

In order to determine the amount of aniline adsorbed by the alumina, a collection of samples is required for building chemometrics model. Since aniline is a pure chemical and the influence of aniline vapor upon NIR-DRS could be neglected in the present experimental setup (the concentration of vaporous aniline is much less than that of adsorbed

aniline), actual samples out of the adsorption process could be simulated simply as follows. Each sample in the collection was prepared by well mixing a given amount of aniline (if merely a little amount of aniline was demanded, its solution of CCl_4 was used, because CCl_4 was NIR-transparent, nonpolar, and able to rapidly evaporate after blending) and a given amount of the alumina together. NIR-DRS of these mixtures were recorded in the same rectangular quartz-cell under the same conditions mentioned above (of course, it is unnecessary to introduce any gas flow).

The baselines of NIR-DRS were first corrected with linear method using OMNIC 5.2a, the accessory software of Nexus 870 FT-IR/NIR spectrometer. Because aniline was a pure chemical, and the alumina, as an inorganic material, scarcely affects NIR-DRS in certain wavenumber ranges, the selection of wavenumber range for building chemometrics model became straightforward. Range of $5600\text{--}6100\text{ cm}^{-1}$ (the first overtone of C–H stretching vibration) was chosen to predict the total amount of aniline in alumina. This range is hardly influenced by the interaction between the aniline molecule and alumina surface, or in other words, whether the aniline is just on the alumina surface or in bulk liquid of aniline, the spectra within this range are the same. As for the range of $6300\text{--}6900\text{ cm}^{-1}$, corresponding to N–H stretching vibration, the situation is different, and we will discuss the subject later in detail.

Partial least squares (PLS) as a popular chemometrics algorithm has been used in NIR research and application for decades (Peussa et al. 2000; Rohe et al. 1999). Our process of building a PLS calibration model was carried out in the conventional leave-one-out cross-validation way. Considering the wide concentration range involved in the adsorption process—the ratio of the highest concentration to the lowest (10^{-4} w/w, i.e., the detection limit of NIR-DRS) usually exceeded 10^3 —a linear model covering the whole concentration range might not be satisfactory. Therefore, we selected following strategy to cope with this problem (Næs and Isaksson, 1992, 1990; Centner and Massart 1998).

A collection of 142 samples were prepared with blending method described above. Of these samples, 51 samples—called “low concentration group”—ranged in concentration from 0.0000 to 0.0100 at intervals of 0.0002 (the concentration of aniline in alumina is represented as the ratio of the aniline to the alumina by weight, g/g), and 91 samples—called “high concentration group”—ranged from 0.0200 to 0.2000 at intervals of 0.0020. The samples in the “low concentration group” are divided into a calibration set and a validation set. The validation set contained one-fourth of the 51 samples (i.e., 13 samples), while other 38 samples were assigned to the calibration set for building the first PLS calibration model (the number of latent factors in the PLS model was three). The samples in the “high concentration group” were treated in the same way to build the second

PLS calibration model (the number of latent factors in the PLS model was also three). The selection of the correct calibration model to obtain predicted value is straightforward for most unknown samples. For some rare borderline samples, i.e., samples within 0.0100–0.0200, the mean of two concentrations predicted by the two models respectively was regarded as the final answer.

The performance of the two models could be judged by samples of their own validation sets in terms of root mean standard error of predication (RMSEP), relative root mean standard error of prediction (RRMSEP) and coefficient of determination (R^2). Here, RMSEP is defined as: $\text{RMSEP} = [\sum(C_P - C_A)^2/n]^{1/2}$, where C_P is the predicted concentration of a sample in the validation set, C_A is the actual or known concentration of the same sample in the validation set, and n is the number of the predicted concentrations; RRMSEP is defined as: $\text{RRMSEP} = \text{RMSEP}/C_M$, where C_M is the mean of the actual concentrations. In order to further evaluate the performance of our chemometrics method, spectra of fourteen samples at adsorption equilibrium states were also recorded and treated with the method to obtain predicted concentrations, while these same samples were later desorbed with thermogravimetry to obtain actual concentrations. These results are shown in Fig. 2. All chemometrics algorithms were programmed with MATLAB 5.0. From the figure, one could assume that the predicted results were acceptable, although when the actual concentration was very low the relative error was somewhat high.

3.2 Study on adsorption equilibrium

With our experimental setup, it is easy to determine whether the adsorption process achieves an equilibrium state according to the change of spectra (the equilibrium state was reached if changes of spectral absorbance within $5600\text{--}6100\text{ cm}^{-1}$ were less than 0.0002 during 10 min). It is worth noting that the NIR probe should be placed over the rearmost part of the alumina in the quartz-cell, since the front part of alumina always achieved equilibrium earlier. Another advantage of our experiment is that the equilibrium could be reached rapidly, for the adsorption process was carried out in flowing gas rather than in static vapor. Figure 3 shows the isotherm at 303.15 K. It obviously belongs to type in terms of the BDDT (Brunauer et al. 1940) classification, in which the adsorbed amount increased greatly with the increase of partial pressure when the partial pressure was low, but increased slowly within the region of large partial pressure.

3.3 Study on adsorption kinetics

Unlike the study of equilibrium, during kinetic study the NIR probe, whose diameter was 3 mm, should be placed

Fig. 2 Correlation plots between the actual and the predicted concentrations of aniline in alumina; (a) samples of the validation set in “low concentration group”; (b) samples of the validation set in “high concentration group” (●) and samples at equilibrium states (+)

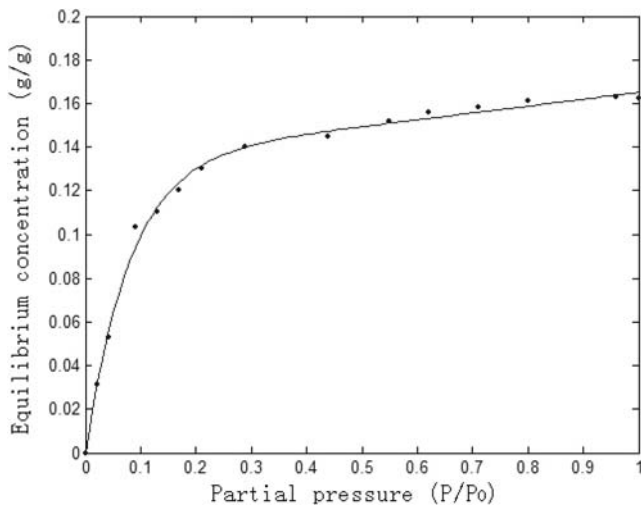
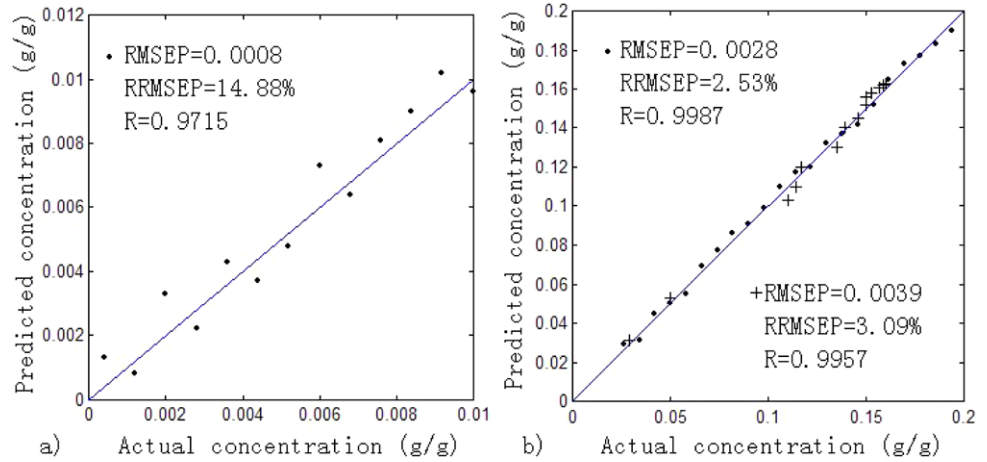


Fig. 3 The isotherm of aniline-alumina adsorption at 303.15 K

appropriately so that the foremost part of alumina in the quartz-cell was covered by NIR radiation. When the volumetric flow rate of influent gas (F_0) was not too small, the concentration of aniline in the gas was not too low, and the sieve (made of stainless steel) before the alumina did not adsorb aniline significantly, the tiny space within 3 mm can be reasonably regarded as a differential adsorption bed (DAB) where each part of alumina contacted with a constant bulk concentration of aniline, namely, the concentration of the aniline in the influent gas, and the adsorption heat was removed quickly by the gas flow for providing an isothermal environment (Do and Do 2001). All these features made treatment of kinetic data in a DAB much more simple and reliable.

Figure 4 shows that the concentration of aniline in alumina increased as the adsorption process went on. Since the interval recording time (about 30 s) is not too long (in fact, our NIR spectrometer can scan 16 times within less than 5 second), instantaneous adsorption rate can be estimated approximately as follows: $R_n = (C_{n+1} - C_n)/t$, where C_n

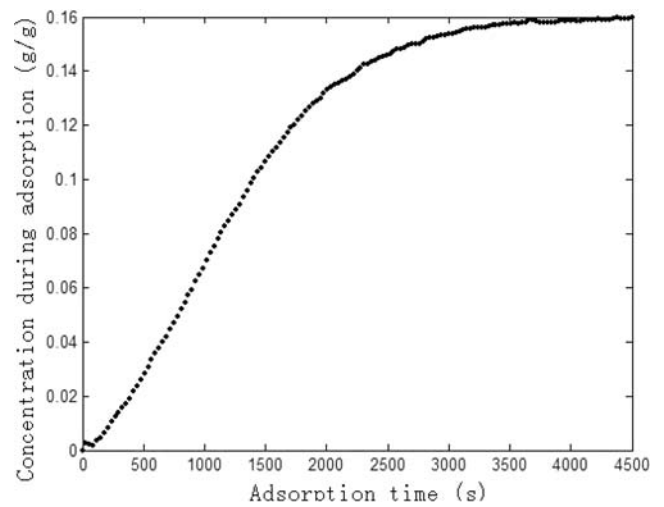


Fig. 4 The concentration of aniline adsorbed by alumina during the process. $T = 303.15$ K; $P/P_0 = 1.00$; $F_0 = 400$ ml/min; intervals of recording time: about 30 seconds

is the concentration at one recording time, C_{n+1} is that at the next recording time, and t is the time passed. Figure 5 demonstrates the relationship between the adsorption rate and adsorption time as well as the concentration of aniline adsorbed by alumina. These relationships are crucial for building a mass transfer model in engineering. Of course, very low concentrations made several data points near the beginning of the adsorption unreasonable and accordingly should be ignored. From Fig. 5, we could know that at the beginning the adsorption rate increased with adsorption time, while decreasing as the adsorption continued. However, the phenomenon is uncommon for physical adsorption, whose adsorption rate usually becomes slow monotonously as time passing. And we will try to explain it with the information about the chemical state aniline on the alumina surface.

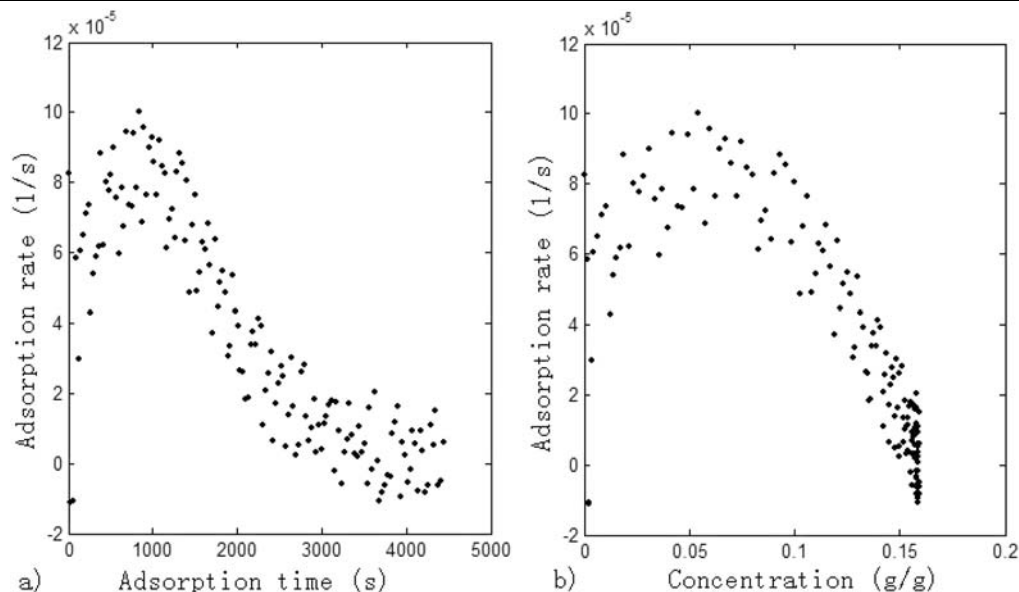


Fig. 5 Correlation between adsorption rate and adsorption time (a); correlation between adsorption rate and the concentration of aniline adsorbed by alumina (b). $T = 303.15$ K; $P/P_0 = 1.00$; $F_0 = 400$ ml/min; intervals of recording time: about 30 seconds

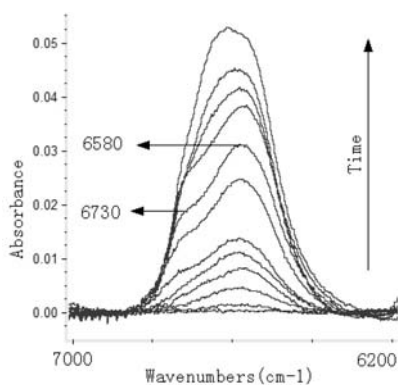


Fig. 6 The NIR-DRS (preprocessed through baseline correction) during the adsorption process. $T = 303.15$ K; $P/P_0 = 1.00$; $F_0 = 400$ ml/min; $t = 0, 347, 574, 809, 1164, 1358, 1539, 1880, 2432, 2708, 3065, 4588$ seconds

3.4 The chemical state of aniline

In order to more clearly demonstrate spectral change in $6300\text{--}6900\text{ cm}^{-1}$ —corresponding to N–H stretching vibration—twelve spectra recorded at different times during the adsorption process were selected and shown in Fig. 6.

As shown in Fig. 6 there were at least two kinds of aniline in the system. The absorption peak at about 6730 cm^{-1} was attributed to the bulk liquid of aniline (the first state of aniline), while the absorption peak at about 6580 cm^{-1} should be assigned to the chemisorption of aniline on alumina surface (the second state of aniline), for the coordination bond between Al and N ($\text{Al}\leftarrow\text{NH}_2\text{C}_6\text{H}_5$) shifted the N–H stretching vibration to longer wavelengths (Amenomiya 1977). This conclusion could also be supported by the spec-

tra of silica gel-aniline adsorption system (the spectra not shown), which had only one peak of N–H stretching vibration. Therefore, the adsorption process could be depicted as follows. At first the aniline was chemically adsorbed on part of the alumina surface as the second state; then it was adsorbed on other parts of the surface continuously, while being adsorbed on the adsorbed aniline layers as the first state simultaneously; and at last when the alumina surface were covered with aniline completely, the aniline would be adsorbed physically as the first state until equilibrium. Furthermore, since the kinetic data in Fig. 5 and spectra in Fig. 6 were obtained synchronously, it would be valuable to combine them for analysis. As mentioned above, Fig. 5 showed an unusual phenomenon in the adsorption process, but it can be explained reasonably by the information of Fig. 6: at the beginning the adsorption was mainly chemisorption, and consequently was relatively slow (generally the activation energy of physisorption is zero, whereas that of chemisorption is higher); as physisorption took place the adsorption rate grew up; and when the alumina adsorbed more and more aniline, the physisorption slowed down naturally and gradually.

Obviously, the experimental setup and procedure designed are appropriate to study adsorption thermodynamics, kinetics and the chemical state of the adsorbate in the adsorbate-adsorbent system simultaneously under various conditions like temperature, the partial pressure, or volume flow rate in laboratory, and also can be possibly transformed into non-invasive monitoring an industrial process, where the quartz-cell containing adsorbent will be replaced by an industrial adsorption bed.

4 Conclusion

With an innovative experimental setup, we have thoroughly studied the uptake of aniline by active alumina through non-invasive monitoring the adsorption process. According to experimental results, the isothermal line belonged to type in terms of the BDDT classification; there were two kinds of adsorption (the chemisorption and physisorption) corresponding to two kinds of aniline chemical state, respectively (aniline adsorbed on alumina surface and aniline in bulk liquid); the two kinds of adsorption did not always take place one after the other but simultaneously during some periods; and the rate of chemisorption is less than that of physical one. What is more important, this paper demonstrates that the method capable of obtaining simultaneous information about thermodynamics, kinetics and the chemical state of the adsorbate molecules in the adsorbent may largely improve our understanding of an adsorption process.

References

- Amenomiya, Y.: Active sites of solid acidic catalysts. *J. Catal.* **46**, 326–330 (1977)
- Blanco, M., Villarroya, I.: NIR spectroscopy: a rapid-response analytical tool. *TrAC, Trends Anal. Chem.* **21**, 4–12 (2002)
- Brunauer, S., Deming, L.S., Deming, W.S., Teller, E.: The study on types of adsorption. *J. Am. Chem. Soc.* **62**, 1732–1740 (1940)
- Cao, D.V., Mohr, R.J., Rao, M.B., Sircar, S.: Self-diffusivities of N₂, CH₄, and Kr on 4A zeolite pellets by isotope exchange technique. *J. Phys. Chem.* **104**, 10498–10506 (2000)
- Centner, V., Massart, D.L.: Optimization in locally weighted regression. *Anal. Chem.* **70**, 4206–4212 (1998)
- Do, D.D., Do, H.D.: Surface diffusion of hydrocarbons in activated carbon: comparison between constant molar flow, differential permeation and differential adsorption bed methods. *Adsorption* **7**, 189–197 (2001)
- Ferreira, A.F.P., Boelens, H.F.M., Westerhuis, J.A.: Inline monitoring of butane isomers adsorption on MFI using near-infrared spectroscopy: drift correction in time based experiments. *Langmuir* **21**, 6830–6838 (2005)
- Graaf, J.M., Kapteijn, F., Moulijn, J.A.: Methodological and operational aspects of permeation measurements on silicalite-1 membranes. *J. Membr. Sci.* **87**, 144–152 (1998)
- Mayfield, P.L.J., Do, D.D.: Measurement of the single-component adsorption kinetics of ethane, butane, and pentane onto activated carbon using a differential adsorption bed. *Ind. Eng. Chem. Res.* **30**, 1262–1268 (1991)
- Mohr, R.J., Vorkapic, D., Rao, M.B., Sircar, S.: Pure and binary gas adsorption equilibria and kinetics of methane and nitrogen by isotope exchange technique. *Adsorption* **5**, 145–152 (1999)
- Næs, T., Isaksson, T.: Locally weighted regression and scatter correction for near-infrared reflectance data. *Anal. Chem.* **62**, 663–672 (1990)
- Næs, T., Isaksson, T.: Locally weighted regression in diffuse near-infrared transmittance spectroscopy. *Appl. Spectrosc.* **46**, 34–43 (1992)
- Peussa, M., Härkönen, S., Puputti, J., Niinistö, L.: Application of PLS multivariate calibration for the determination of the hydroxyl group content in calcined silica by DRIFTS. *J. Chemom.* **14**, 501–507 (2000)
- Rohe, T., Becker, W., Kölle, S., Eisenreich, N.: Near infrared (NIR) spectroscopy for in-line monitoring of polymer extrusion processes. *Talanta* **50**, 2283–2291 (1999)
- Rynders, R.M., Rao, M.B., Sircar, S.: Isotope exchange technique for measurement of gas adsorption equilibria and kinetics. *AIChE J.* **43**, 2456–2463 (1997)
- Sircar, S.: Recent developments in macroscopic measurement of multicomponent gas adsorption equilibria, kinetics, and heats. *Ind. Eng. Chem. Res.* **46**, 2917–2923 (2007)
- Sun, L.M., Zhong, G.M., Gray, P.G., Meunier, F.: Frequency response analysis for multicomponent diffusion in adsorbents. *J. Chem. Soc., Faraday Trans.* **90**, 369–376 (1994)
- Workman, J. Jr., Koch, M., Veltkamp, D.J.: Process analytical chemistry. *Anal. Chem.* **75**, 2859–2882 (2003)
- Xomeritakis, G., Tsai, C.Y., Jeffrey, C.B.: Microporous sol-gel derived aminosilicate membrane for enhanced carbon dioxide separation. *Sep. Purif. Technol.* **42**, 249–256 (2005)
- Yasuda, Y., Matsumoto, K.J.: Straight- and cross-term diffusion coefficients of a two-component mixture in micropores of zeolites by frequency response methodology. *J. Phys. Chem.* **93**, 3195–3201 (1989)
- Zhang, H., Lee, T.: A novel silica gel adsorption/near-infrared spectroscopic method for the determination of hexanal as an example of volatile compounds. *J. Agric. Food Chem.* **45**, 3083–3090 (1997)