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How accessible is the specific surface area of minerals? A comparative study with Al-containing minerals as model substances

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ABSTRACT

The specific surface area (SSA) is a principal characteristic for the assessment of the sorption capacity of minerals. In addition to size, the accessibility of the surface area is of importance, which is primarily affected by porosity. In particular the micropore surface area of soil minerals may be inaccessible due to too small pore entrances or their clogging by organic material. In this study, SSA and micropore surface area of three minerals (Al oxide, Al hydroxide and kaolinite), acting as model materials for oxides, hydroxides and clay minerals, respectively, were measured by gas adsorption methods with both N_2 at 77.35 K or CO_2 at 273.15 K and the retention of the polar liquid ethylene glycol monoethyl ether (EGME). Moreover, porosity was assessed by ^{129}Xe nuclear magnetic resonance (NMR) spectroscopy. A NaY zeolite was used as microporous reference material. ^{129}Xe NMR spectroscopy and the determination of SSA by physisorption of N_2 (BET-N_2 SSA) were performed after sample pretreatment at various outgassing temperatures because BET-N_2 SSA and porosity are significantly affected by the outgassing temperature due to the loss of adsorbed water molecules. For all minerals investigated, the highest SSA was obtained by EGME retention. The gas adsorption methods exhibited differences in SSA and micropore surface area depending on the gas and pretreatment temperature. Thereby, increased pretreatment temperatures resulted in increased SSA and micropore surface area. ^{129}Xe NMR spectra revealed that this increase in surface area was mainly ascribed to an increase in porosity. It appeared that the accessibility of surface area was limited by surface hydration. This implies that at environmental conditions, partly saturated pores will yield a reduced sorption capacity compared to the one that may be expected from SSA measurements. Consequently, porosity and hydration of the mineral surfaces have to be considered for an improved assessment of the sorption capacity of minerals and soils.

1. Introduction

The specific surface area (SSA) of a solid is a basic property which essentially affects its reactivity as a catalyst or a sorbent (Davis and Kent, 1990; Feller et al., 1992). The larger the SSA, the more surface sites are available, resulting in a higher reactivity or sorption capacity of the solid. In case of porous solids, a large part of the SSA may be present inside pores as pore surface area (e.g., Gregg and Sing, 1967). Thereby, their accessibility determines whether these parts of the SSA participate in the reaction or not. This is governed by the size and the shape of the pores.

According to the International Union of Pure and Applied Chemistry (IUPAC), pores are classified depending on the pore diameter into macropores (>50 nm), mesopores (2–50 nm) and micropores (<2 nm) (e.g., Davis and Kent, 1990; Sing et al., 1985). Especially for micropores, the accessibility of the pore surface area to potential adsorptives may be limited because of size exclusion. But even for larger

pores, the adsorptives may not be able to enter the pore due to the shape of the pore. For instance, the pore entrance of a bottle-neck shaped pore may be too small to allow passage of the adsorptives, although its average pore size would be large enough. Accordingly, in particular the size of the pore entrance is decisive for the accessibility of the pore surface area.

Soils play an important role in the cycling of water and elements because of their ability to retain nutrients and pollutants. They consist of a complex mixture of minerals and organic material, whereof especially clay minerals and pedogenic oxides and hydroxides provide substantial SSA and thus contribute significantly to the sorption capacity of soils (e.g., Dümig et al., 2012; von Lützow et al., 2006). Therefore, the SSA is considered as a basic parameter and has been determined frequently. However, the interpretation of the results may be complicated because of the interaction of the individual soil particles, resulting in the formation of organo-mineral associations and aggregates in various sizes (e.g., Bronick and Lal, 2005; von Lützow et al., 2006). Many studies observed an increase of SSA of soils after the removal of organic matter (Feller et al., 1992; Pennell et al., 1995; Theng et al., 1999; Zimmermann et al., 2007). This was explained by the coating of mineral surfaces with organic matter, making them inaccessible for the probing molecules (Kaiser and

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Guggenberger, 2003, 2007; Mikutta et al., 2004; Theng et al., 1999; Zimmermann et al., 2007). Especially the clogging of pore entrances by organic matter may lead to a significant reduction of the SSA (Kaiser and Guggenberger, 2003, 2007; Mikutta et al., 2004; Theng et al., 1999). Consequently, in soil materials, the accessibility of pore surface area can also be limited by the clogging of pore mouths with organic matter.

The common method for the determination of SSA of soils is physisorption of nitrogen gas at 77.35 K according to the method of Brunauer et al. (1938). As the nitrogen molecule has a permanent quadrupolar moment and thus acts as a polar probe (Bartoli et al., 2007), it has a high affinity for mineral surfaces and cannot probe the hydrophobic regions of organic materials (Kaiser and Guggenberger, 2003; Ravikovitch et al., 2005), which causes the effect described above. Therefore, in addition, the use of other methods has been proposed, including the use of CO_2 as probing molecule or the adsorption of polar liquids like ethylene glycol and ethylene glycol monoethyl ether (EGME). CO_2 molecules are more prone to enter small pores and the microporous matrix of organic materials due to the higher temperature during measurement (normally 0 °C or room temperature) compared to N_2 (de Jonge et al., 2000; de Jonge and Mittelmeijer-Hazeleger, 1996; Echeverría et al., 1999; Ravikovitch et al., 2005). Polar liquids are also able to probe the so-called internal surface area, i.e., interlayer surfaces of clay minerals and micropore surface area of organic matter (de Jong, 1999; Tiller and Smith, 1990; Yukselen-Aksoy and Kaya, 2010). Consequently, the various methods yield different results for SSA and micropore surface area.

The aim of this study was to evaluate the accessibility of SSA and micropore surface area of minerals that contribute significantly to the SSA of soils. For this purpose, the SSA and micropore surface area of selected pure minerals, acting as model materials, were determined by gas adsorption methods with both N_2 at 77.35 K or CO_2 at 273.15 K and the retention of the polar liquid EGME. Moreover, the porosity was assessed by ^{129}Xe nuclear magnetic resonance (NMR) spectroscopy because xenon atoms have been shown to be a very sensitive probe for studying porous solids, as their chemical shift depends among others on Xe-surface interactions and may yield information on pore size and shape (Barrie and Klinowski, 1992; Filimonova et al., 2004; Magusin et al., 1997). As model materials, an Al oxide, an Al hydroxide and a kaolinite were selected to represent oxides, hydroxides and clay minerals, respectively. Iron containing minerals were not studied in order to avoid possible effects on the chemical shift by paramagnetic iron (Filimonova et al., 2006; Springuel-Huet et al., 1999). In addition, a NaY zeolite was used as microporous reference material. ^{129}Xe NMR spectroscopy and the determination of SSA by physisorption of N_2 (BET-N_2 SSA) were performed after sample pretreatment at various outgassing temperatures because several studies had reported that the BET-N_2 SSA is significantly affected by the outgassing temperature due to the loss of adsorbed water molecules during pretreatment (e.g., Aldcroft et al., 1968; Aylmore et al., 1970; Brooks, 1955; Clausen and Fabricius, 2000; Kaufhold et al., 2010) in particular from micropores (Metz et al., 2005). The different extend of loss of water was also expected to have an impact on the porosity of the samples probed by xenon gas. The integration of the different results will shed more light on the accessibility of the SSA of minerals. This may have implications for evaluating the SSA of minerals and soils in general, since hydration state was not considered so far to affect SSA and thus sorption capacity under field conditions in such extend.

2. Materials and methods

2.1. Minerals

In this study, four different commercially available Al-containing minerals were investigated: a zeolite (NaY zeolite, product number 334448; Sigma-Aldrich, Saint Louis, MO) that was used as a microporous reference material, an Al oxide (Alumina Type 150, BAM-PM-104; Federal Institute for Materials Research and Testing, Berlin, Germany), an Al hydroxide

(Apyral 60; VAW Aluminium AG, Bonn, Germany) and a kaolinite (Kick-Tec 2; Kaolin- und Quarzsandwerke GmbH & Co, Schnaittenbach, Germany). All materials were used as received.

2.2. Sample characterisation

The purity of the minerals was assessed by measuring the total C and N contents by means of dry combustion at 975 °C using an elemental analyser (Hekatech Euro EA 3000, Wegberg, Germany). In addition, X-ray diffraction (XRD) measurements were performed for mineralogical analysis. XRD patterns were obtained using a Philips PW 1050 diffractometer (Philips, Eindhoven, The Netherlands) equipped with a diffracted-beam graphite monochromator and a Bruker AXS microdiffractometer equipped with a General Area Detection Diffraction System (GADDS) detector. $CoK\alpha$ X-ray radiation was applied at 40 kV and 25 mA. Samples were prepared as randomly oriented powder specimens and measured from 5°2Θ to 80°2Θ in steps of 0.02°2Θ with a counting time of 5 s for each increment.

2.3. Surface area and porosity measurements

All measurements of the surface area by means of gas adsorption (N_2 and CO_2) were performed in duplicate with a Quantachrome Autosorb 1 analyser (Syosset, NY).

N_2 physisorption was conducted at 77.35 K by measuring 25 ad- and 39 desorption points in the p/p^0 range between 0.025 and 0.995, and the BET-N_2 SSA was calculated from 11-point adsorption isotherms in the relative pressure range between 0.05 and 0.30 according to the Brunauer–Emmett–Teller (BET) equation (Brunauer et al., 1938). The surface area of the micropores was assessed by the t-method of de Boer et al. (1966). In a so-called t-plot, the volume of gas adsorbed is plotted versus the statistical thickness of the adsorbed film, t, that is calculated by the de Boer equation (de Boer et al., 1966). From the t-plot, the micropore volume and the external surface area of the sample can be derived, and the micropore area can be calculated from the difference between the BET-N_2 SSA and the external surface area (Michot and Villiéras, 2006).

Prior to analysis, the samples were outgassed under vacuum at either 40 °C or 105 °C in order to remove adsorbed volatile substances like water vapour. Outgassing time was at least overnight, depending on the size of surface area present. Before termination of the outgassing procedure, it was checked by means of a test procedure of the instrument software, whether outgassing was sufficient. Residual pressures were in the range of $0.67–1.33 \times 10^{-2}$ mbar or even lower.

The C constant is a dimensionless constant included in the BET equation and is related to the enthalpy of the nitrogen gas on the sample surface (Davis and Kent, 1990; Mayer, 1999; Pronk et al., 2011). In this study, C constants were determined in order to assess the microporosity and to complement the BET-N_2 SSA values because low C constants (<20) increase the uncertainty in the calculation of the SSA (Sing et al., 1985). As the use of the entire BET isotherm can lead to large errors in the C constant (Mayer, 1999), the C constant was calculated from the residual between the measured partial pressure points and the BET isotherm according to the procedure described by Mayer (1999). These residuals show normally an N-shaped pattern. Only the three to five points of the steepest part of the isotherm, which are typically situated in the mid-range of partials pressures, were selected for the calculation.

CO_2 adsorption isotherms were obtained by measuring 20 points in the p/p^0 range between 3×10^{-5} and 3×10^{-2} at 273.15 K. Micropore surface area was calculated according to the Dubinin–Radushkevich (DR) equation (Dubinin and Radushkevich, 1947). Sample pretreatment was similar to the N_2 physisorption measurements, but only conducted at 40 °C. Likewise, outgassing times were at least overnight and residual pressures at the end of the outgassing period were in the range of $0.67–1.33 \times 10^{-2}$ mbar or even lower.

Complementary to the gas adsorption methods, the SSA was also determined by adsorption of the polar liquid EGME (EGME SSA). In this