Basicity and Porosity of a Calcined Hydrotalcite-Type Material from Nitrogen Porosimetry and Adsorption Microcalorimetry Methods

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The hydrothermal transformation at 90–95 °C of a slurry of Al₂O₃/MgO/(CH₃COOH)/H₂O with molar oxide composition 1:4:4:2:1:1111 produced a hydrotalcite-like (HT) material free from phase impurities and having an approximate unit cell composition of Mg₅₋ₓAlₓ(OH)₂₋ₓ(CHCOO)ₓ0.33. ¹³C NMR and ²⁷Al NMR spectra have revealed that the air-dried solid contains acetate anions probably as charge-compensating anions in the HT interlamellar space and that all the aluminum is present in octahedral coordination. After calcination in air at 500 °C, the stacks of brucite layers that form the HT crystals exfoliate, forming a stable mesoporous “house-of-cards” structure with pore width in the range 2.5–20.0 nm, characterized by a DFT surface area of 254 m²/g and total pore volume of 0.33 cm³/g at 0.995 p/Po, that is available to sorption and catalysis. A 5-h exposure to 100% steam at 760 °C collapses the HT material forming a residue that contains a well-crystallized MgO and an Al spinel phase identified by XRD. At 30 °C, adsorption microcalorimetry with SO₂ revealed that the calcined HT material behaves like a solid base possessing a large (530 μmol SO₂/g) population of basic sites with strength near 170 kJ/mol; the strength of the strongest basic site is 190 kJ/mol. The steam-aged HT retains the strength of its strongest basic sites but loses most of its sorption capacity for SO₂. Thus, materials of this type should be efficient adsorbents for the removal of sulfur oxides and other acidic air pollutants in industrial applications that do not require the abovementioned hydrothermal stability.

Introduction

Hydrotalcite is a naturally occurring mineral¹–³ with typical composition Mg₆Al₂(OH)₁₆CO₃·4H₂O consisting of stacks of brucite-like layers in which Mg(VI) atoms are replaced in part by Al(VI) atoms, thus generating sheets having a net positive charge that is compensated by interlamellar anions. Although, in principle, any anion could be placed in the interlamellar space, carbonates are the anions commonly found in naturally occurring materials. Hydrotalcite-like compounds are layered double hydroxides (LDHs) with the general formula: [MIIₓ₋ₓ−MIIIₓ(OH)ₓ]₂₋ₓ[Aₓ₋ₓ²₋ₓ⁻Zₓ₋ₓ⁻nH₂O where MII is a divalent cation (such as Mg, Ca, Mn, Fe, Co, Cu, Zn, and Ni) and MIII is a trivalent cation (such as Al, Cr, Mn, Co, Ni, La, and Fe) and A is the charge compensating anion.⁴,⁵ Divalent and trivalent cations are randomly distributed in the brucite-like layer; the charge of LDHs is controlled by the degree of isomorphous substitution of MII by MIII cations while the charge density distribution is controlled by the distribution of MIII ions in the octahedral layers.⁵ A unique characteristic of these layered materials is their ability to reconstruct their layered structure, lost on heating at a temperature not exceeding 400 °C, when exposed to the desorbed solvent; this property is lost at 500 °C.⁴

In contrast to smectites,⁶ hydrotalcites and synthetic hydrotalcite-like materials are referred to as anionic days owing to their ability to exchange charge-compensating interlamellar anions with a variety of organic and inorganic anions.⁷ As a result, it is possible to generate LDHs with a variety of properties. Of particular interest is the reported use of LDHs in the preparation of fluid cracking catalysts (FCCs) for the conversion of sulfur-containing feedstocks.⁸ A detailed review of the synthesis, characterization, and physicochemical characteristics of LDHs is in ref 4.


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It is the purpose of this paper to report our examination of the porous structure and basic properties of a synthetic hydrotalcite-like sample after calcination in air at 500 °C and after 5 h of steam-aging at 760 °C with 100% steam to simulate the aging of FCCs at microactivity test conditions.

Experimental Section

Materials Preparation. A hydrogel of composition Al₂O₃/(CH₃COOH)H₂O (0.1:0.22:27.8) was prepared by slurring pseudoboehmite (Catapal B) in a diluted acetic acid solution according to a published procedure. After heating the hydrogel (with stirring) at 60 °C for 1 h, a second slurry of MgO/H₂O (0.44:8.3) prepared by suspending MgO (99.95%, -325 mesh powder) from Al₂O₃ was added to the hydrogel, and the resulting mixture was heated at 90–95 °C overnight (with stirring) in a round-bottom flask equipped with condenser and stirring mechanism. This procedure has been described in detail elsewhere. The solid was recovered by filtration under vacuum, washed with an excess of hot (60 °C) DI water, and then allowed to dry at 25 °C in a desiccator overnight. The pristine material was then calcined in flowing air at 500 °C (calcined sample) and exposed for 5 h to 100% steam at 760 °C (steam-aged sample). Therogravimetric analysis was performed with a TG-DSC 111 Setaram instrument using a heating rate of 5 °C/min and 0.42 cm³/s of an air/He mixture performed with a TG-DSC 111 Setaram instrument using a heating rate of 5 °C/min and 0.42 cm³/s of an air/He mixture as a purge gas. X-ray powder diffraction (XRD) spectra were obtained with Cu Kα radiation using a Philips PW 3710/3020 diffractometer equipped with a monochromator. The measurements were made using a step scanning program with 0.02° per step and acquisition time of 5 s per step.

Nitrogen Porosimetry. Nitrogen sorption isotherms obtained at liquid nitrogen temperature were collected over a wide pressure range using a volumetric technique on a Micromeritics ASAP 1010 adsorption instrument. Prior to analysis, samples weighing from 0.1 to 0.3 g were outgassed in a vacuum at 250 °C for at least 16 h; for the air-dried HT sample degassing was performed at 100 °C to avoid decomposition of acetate anions. The total pore volume (PV) was derived from the amount of nitrogen adsorbed at a relative pressure close to unity (p/po = 0.995) by assuming that all the accessible pores were then filled with liquid nitrogen. p is the equilibrium pressure and po is the saturated vapor pressure of the adsorbate at the temperature of the experiment. Surface area (SA) measurements were performed using the Brunauer–Emmett–Teller (BET), Langmuir, and Barret–Joyner–Halenda (BJH) equations and compared with results obtained with DFT methods. DFT data refer to cylindrical pore widths equal to or less than 33.4 nm. The total surface area reported in Tables 1 and 2 was determined from the cumulative areas of unfilled pores larger than 33.4 nm, which is given by the DFT analysis.

Solid State NMR. ²⁷Al MAS NMR spectra were obtained at 130.2 MHz, using a Bruker Avance (DSX) 500 spectrometer. Samples were spun in cylindrical 4-mm zirconia rotors at a spinning frequency of 12 kHz. The spectra were recorded with short pulses of 2 μs (flip angle ≈45°) and relaxation delays of 1 s. Resonance shifts are reported using liquid samples of 1 M aqueous solutions of Al(NO₃)₃ as external reference standard.

Figure 1. X-ray diffractograms for (A) HT crystals at 25 °C; (B) HT crystal after calcination in air at 500 °C; and (C) HT crystals after steam aging (760 °C, with 100% steam).

Results and Discussion

The hydrothermal transformation at 90–95 °C/10 h of a slurry of Al₂O₃/MgO/(CH₃COOH)/H₂O with molar oxide composition 1:4.4:2.2:1110 produced a hydro-talcite-like material essentially free from phase impurities such as unreacted MgO or Al₂O₃. Figure 1 (middle). This solid was found to contain small amounts of Ca and Na (0.4% CaO and 1.0% Na₂O) probably associated with impurities in the reactants used. Elemental analysis of the reaction product gave Mg/Al = 2.1 and Al/(CH₃COO) = 1.02 consistent with an approximate unit cell composition of Mg₀.₆₆Al₀.₃₃(OH)₂(CHCOO)₀.₃₃ in agreement with published results and indicating that the aforementioned hydrothermal reaction is almost stoichiometric.

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produces a well-crystallized spinel, MgAl$_2$O$_4$\(^{15}\) together with some MgO\(^{16}\); see Figure 1 (top). The weak lines near $2\theta = 11.3^\circ$, 22.8$^\circ$, 34.7$^\circ$, and 39.1$^\circ$ in Figure 1 (top) are consistent with the presence of minor amounts of magnesium aluminum hydroxide hydrate\(^{17}\). Micrometer-scale scanning electron micrographs (SEM) show that the air-dried HT sample is initially composed of a loose agglomeration of wavy sheets irregular in size and shape, Figure 2 (top). The sample surface topography does not change appreciably after calcination at 500 °C, Figure 2 (middle). However, after steam-aging it is possible to observe the formation of rigid and flat plates covered by a second phase having a needle-like appearance, Figure 2 (bottom).

**Thermogravimetric Analysis.** Thermograms in Figure 3 indicate that the sample under study maintains a constant weight up to 50 °C, and then an evolution of weakly bonded water begins that is completed at 260 °C. Near this temperature the interlayered acetate anions start to decompose, and in the 260–450 °C temperature range, the DTG profile shows the existence of a broad endotherm with a peak minimum near 300 °C and a weak shoulder near 360 °C associated with the decomposition and thermal desorption of acetate fragments in the interlamellar space. When heating is repeated in helium (not shown) instead of air, the thermograms (TG and DTG) obtained are indistinguishable.

**The Density Functional Theory.** Several adsorption theories are available to extract SA and PV information from experimental adsorption isotherms. The Langmuir and BET formalisms are based on the model of adsorption on a free surface. The Langmuir model assumes the surface saturates after the first adsorbed layer, whereas the BET model presumes that multilayers can form at higher pressures. However, neither model allows for the filling of micropores. Surface areas derived from these two models will differ from the actual area in a way that depends on the solid microporous structure. In contrast, the density functional theory approach treats experimental isotherms as the summation of sorbate uptake, at a given pressure, in pores of variable size $H$. As a result, the integral equation of isothermal adsorption for the case of distributed pore sizes can be written as the convolution\(^{13}\)

$$Q(p) = \int dH q(p,H) f(H)$$

(1)

where $Q(p)$ is the total quantity of adsorbate per gram of adsorbent at pressure $p$ in pores $H$ distributed over the entire micro–meso–macro range; $q(p,H)$, the kernel function, describes the adsorption isotherm for an ideally homoporous material characterized by pore width $H$ as quantity of adsorbate per square meter of pore surface, and $f(H)$ is the desired pore surface area distribution function with respect to $H$.\(^{14}\) Because we are only interested in the numerical values of $f(H)$, we can rewrite eq 1 as a summation

$$Q(p) = \sum q(p,H_i)f(H_i)$$

or in matrix notation $Q = qf$ (2)

where $Q(p)$ is an experimental adsorption isotherm interpolated onto a vector $p$ of pressure points; $q(p,H_i)$

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is a matrix of values for quantity adsorbed per square meter, each row calculated for a value of H at pressures p, and f(Hi) is the solution vector whose terms represent the area of surface in the sample characterized by each pore width Hi. Using the set of hybrid models constructed as described elsewhere13,14 as the function q(p, Hi) and the experimental adsorption isotherm for the function Q(p), eq 2 can be solved for the distribution vector f(Hi). The resulting distributions of pore area and pore volume as a function of pore width are shown later in Figures 7–9.

In addition to pore area and pore volume distributions, adsorption isotherms can provide information on the energetic heterogeneity of surfaces.13 In fact the integral equation of adsorption can be rewritten as

$$Q(p) = \int d\epsilon q(p, \epsilon) f(\epsilon)$$

(3)

where Q(p) has the same meaning as in eq 1; q(p, \epsilon) is the local isotherm used to describe the sorbate uptake (per unit area) on a homotattic surface18 having interaction energy \epsilon, and f(\epsilon) is a function that represents the distribution of surface area with energy \epsilon. DFT is used to calculate values of q(p, \epsilon), and together with the use of the proper numerical methods, model isotherms thus generated can be used to invert the discretized form of the integral equation of adsorption and obtain the adsorptive potential distribution of the adsorbent from experimental adsorption isotherms; details of this procedure can be found elsewhere.13 Results are in Figure 4.

**Nitrogen Porosimetry Results.** As anticipated, the pristine HT sample dried at 25 °C in air has a low DFT surface area of 17 m²/g and it is essentially void of measurable microporosity because the interlayered space is occupied by charge-compensating acetate anions. The small pore volume of 0.024 cm³/g reported in Table 1 is attributed to voids between stacks of brucite layers. As a result, adsorption isotherms for a nonporous material of this type can provide information on the surface adsorptive energies. Distribution of adsorptive energy plots could help in the identification of surface debris, variation in chemical composition, and structural variations.

**Table 1. Surface Area and Pore Volume Results from Nitrogen Porosimetry Data FOR the Pristine HT Sample Dried in Vacuum at 80 °C**

<table>
<thead>
<tr>
<th>method</th>
<th>micro. surface area (m²/g)</th>
<th>total surface area (m²/g)</th>
<th>micro. pore volume (33.4 nm)</th>
<th>pore volume (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DFT</td>
<td>0.0</td>
<td>17</td>
<td>0.0</td>
<td>0.024</td>
</tr>
<tr>
<td>BET</td>
<td>22</td>
<td>22</td>
<td>0.0</td>
<td>0.024</td>
</tr>
<tr>
<td>Langmuir</td>
<td>14</td>
<td>14</td>
<td>0.0</td>
<td>0.019</td>
</tr>
<tr>
<td>BJ H</td>
<td>17</td>
<td>17</td>
<td>0.0</td>
<td>0.019</td>
</tr>
</tbody>
</table>

° Total PV measured at p/Po ~ 0.995 = 0.027.
defects of the HT surface. Plots of surface energy distribution in Figure 4 (bottom) show that the degree of heterogeneity of the pristine, air-dried, HT surface is not high. Surface area with $\frac{q_m}{k_B}$ 33 K is assigned to the oxygens of the brucite layer. After thermal and hydrothermal treatment, the degree of heterogeneity of the HT increases, probably the result of the dehydroxylation of the brucite layers and formation of an Al spinel and MgO mixture; see Figure 4 (top and middle). Surface area with an average $\frac{q_m}{k_B}$ of 42 K in Figure 4 is assigned to the oxygens of the dehydroxylated brucite layers. Higher energy areas having $\frac{q_m}{k_B}$) > 74 K and 80–95 K are attributed to sorption of nitrogen molecules in cavities resulting from the agglomeration of clay platelet aggregates and to quadrupolar interactions of nitrogen with charged sites, respectively. In Figure 4, $\epsilon$ is the Lennard–Jones interaction potential of the adsorbptive with the surface and $k$ is Boltzmann’s constant; $\epsilon/k_B$ has unit of degree Kelvin and is related to the isosteric heat of adsorption.13 The corresponding sorption isotherms are in Figures 5 and 6.

After removing the acetate anions by heating in air at 500 °C/2 h, the clay total DFT SA increases to 254 m$^2$/g from 17 m$^2$/g (Table 2). The isotherm in Figure 5 for the calcined HT closely resembles a type II isotherm; nitrogen uptake monotonically increases with p/Po values due to sorption in the HT mesopores. The same data are plotted on a semilog scale in Figure 6. It is shown that even in the very low pressure region near $10^{-7}$ p/Po nitrogen sorption occurs, although below a relative pressure of $10^{-1}$ the uptakes of nitrogen are low, a result that can be attributed to the few small mesopores present. Above $10^{-1}$ p/Po sorption in the sample’s larger mesopores cause the rapid uptake of nitrogen seen in Figure 6. The cumulative pore area data are in Figure 7. The calcined sample contains a very small amount of micropores with pore width smaller than 0.75 nm. In the 0.75–2.4 nm range the cumulative pore area remains unchanged and starts to increase again for pore width larger than 2.4 nm. The change in the cumulative pore volume is plotted as a function of pore width in Figure 8. The calcination in air of the HT sample produces a mesoporous residue where the pore volume is mainly contained in pores widths larger than 2.4 nm. At 33 nm the cumulative pore volume is 0.18 cm$^3$/g. The differential PV vs pore width profile in Figure 9 is clearly asymmetric with peak maximum near 3.7 nm owing to the predominant presence of pore width in the 3.0–6.0 nm range. Thus, results in Figures 7–9 collectively indicate that a distinguishing feature of this porous solid is the presence of negligible amounts of surface area and pore volume in the micropore region.

for the mesoporous solid under study the Langmuir, BET, and the BJH methods yield surface area values that do not deviate greatly from DFT results (Tables 1–3). However, only the DFT method allows us to extract from adsorption data a much more complete description of a porous material than traditional methods; see Figures 7–9.

**NMR Results.** The comparison in Figure 10 of $^{13}$C CP NMR spectra of reference sodium acetate and air-dried (at 25 °C) HT crystals clearly show that the HT under study contains the expected charge-compensating acetate anions. The corresponding $^{27}$Al NMR spectra of the same HT sample before and after thermal treatments are shown in Figure 11. As anticipated, the spectrum of the air-dried HT exhibits a single resonance (near 9.7 ppm) representing octahedrally coordinated framework Al(VI) species, Figure 11A. On calcination at 500 °C in air, the stacks of brucite layers that form the HT lattice exfoliate and form a “house of cards” structure containing both Al(VI) and tetrahedrally coordinated Al(IV) species represented by resonances at 13.0 and 76.8 ppm respectively (Figure 11B). After steam-aging, the Al(VI) resonance shifts to 11.4 ppm, and the relative intensity of the Al(IV) resonance

**Table 3. Surface Area and Pore Volume Results from Nitrogen Porosimetry Data for the Steamed HT Sample**

<table>
<thead>
<tr>
<th>Method</th>
<th>Micro. Surface Area (m²/g)</th>
<th>Total Surface Area (m²/g)</th>
<th>Micro. Pore Volume (3.34 nm) (cm³/g)</th>
<th>Total Pore Volume (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DFT</td>
<td>4</td>
<td>87</td>
<td>0.0016</td>
<td>0.10</td>
</tr>
<tr>
<td>BET</td>
<td>104</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Langmuir</td>
<td>105</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BJH</td>
<td>91</td>
<td></td>
<td>0.14</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Total PV measured at p/Po = 0.995 = 0.32.
Table 4. SO2 Chemisorption Data at 30 °C (p = 0.2 Torr)

<table>
<thead>
<tr>
<th>sample</th>
<th>( V_T )</th>
<th>( V_r )</th>
<th>( V_{irr} )</th>
<th>initial heat (kJ/mol)</th>
<th>integral heat (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HT, 25 °C</td>
<td>151</td>
<td>18</td>
<td>133</td>
<td>152</td>
<td>13.5</td>
</tr>
<tr>
<td>HT, 500 °C</td>
<td>981</td>
<td>92</td>
<td>889</td>
<td>190</td>
<td>141.0</td>
</tr>
<tr>
<td>HT, 500 °Ca</td>
<td>689</td>
<td>64</td>
<td>625</td>
<td>199</td>
<td>109.0</td>
</tr>
<tr>
<td>HT, steamed</td>
<td>272</td>
<td>33</td>
<td>239</td>
<td>198</td>
<td>37.0</td>
</tr>
</tbody>
</table>

\( a \) Chemisorption at 80 °C.

Table 5. Site Population Distribution (in \( \mu \)mol SO2/g) at 30 °C

<table>
<thead>
<tr>
<th>sample</th>
<th>basic site strength in kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>HT, 25 °C</td>
<td>&lt;100, 100–120, 120–150, 150–200</td>
</tr>
<tr>
<td>HT, 500 °C</td>
<td>85, 17, 40, 100, 120–150, 150–200</td>
</tr>
<tr>
<td>HT, 500 °Ca</td>
<td>155, 45, 251, 530</td>
</tr>
<tr>
<td>HT, steamed</td>
<td>76, 54, 84, 475</td>
</tr>
</tbody>
</table>

\( a \) Chemisorption at 80 °C.

Figure 12. SO2 sorption isotherms for HT samples after (A) air drying at 25 °C, (B) calcination at 500 °C, and (C) steam aging at 760 °C with 100% steam.

Figure 13. Differential heats profiles for HT samples after: A) Air drying at 25 °C, B) Calcination at 500 °C, and C) Steam aging at 760 °C with 100% steam.

Summary and Conclusions

The hydrotalcite-like material described in this paper is particles formed by the long-range stacking of

in a vacuum at 30 °C. By subtracting the adsorbed volume of the secondary isotherms (\( V_T \)) from that of the primary isotherms (\( V_r \)) at the same equilibrium pressure (p = 0.2 Torr), it is possible to obtain \( V_{irr} \), the volume of irreversibly chemisorbed SO2. This value is believed to correlate with the presence of strong basic sites. In Table 4, initial heats have been associated with the strength of the strongest adsorption sites present. On the other hand, integral heats represent the total heat of SO2 adsorption evolved at p = 0.2 Torr and are therefore associated with the solid’s density of basic sites.

At 30 °C the interlamellar space of the hydrotalcite structure is occupied by acetate anions and sites for SO2 chemisorption are not available, thus explaining the low basic sites density and strength exhibited by this material; see Tables 4 and 5 and the differential heat curve in Figure 13. On calcination at 500 °C/2 h in air, the brucite layers that form the calcined HT with 254 m²/g surface area and a house of cards structure available to SO2 chemisorption.

Thus, the calcined HT with 254 m²/g surface area and a house of cards structure available to SO2 chemisorption.

To compare the present results with those obtained with other solid-bases, the SO2 chemisorption temperature was raised to 80 °C from 30 °C. Results in Tables 4 and 5 show the anticipated decrease in SO2 sorption capacity at the higher temperature. At 80 °C, the initial heat of SO2 chemisorption (199 kJ/mol) is 5 kJ/mol greater than the one reported for alumina but lower than the one (215 kJ/mol) measured on magnesia.

Thus, the calcined HT with 254 m²/g surface area and 0.33 cm³/g pore volume (at p/P0 = 0.095) is a solid base in which the strength of the strongest basic sites is greater than the one found in TiO2, Sn/TiO2, SnO2, Ga2O3, Ga/Al2O3, and NaY. After steaming, the steam-aged material suffers a drastic reduction in basic sites density resulting from the collapse of the solid’s porous structure and the formation of an MgAl2O4-MgO mixture; see Tables 3 and 4.

brucite layers in which the positive interlamellar charge, resulting from the isomorphous substitution of Mg with Al atoms, is compensated by acetate anions. The presence of acetate anions has been confirmed by $^{13}$CP NMR carbon results. Moreover, $^{27}$Al NMR spectra indicate that only Al(VI) is present, while chemical analysis reports an Al/\([\text{CH}_3\text{COO}]\) molar ratio of 1.02, lending support to the proposition that the layer net positive charge is indeed compensated by acetate anions.

The decomposition at 500 °C in air of interlamellar charge-compensating acetate anions causes the delamination (exfoliation) of the stacks of brucite layers and the formation of a mesoporous house-of-cards structure with DFT surface area and pore volume of 254 m$^2$/g and 0.18 cm$^3$/g, respectively. This mesoporous solid behaves like a solid-base sorbing 689 $\mu$mol SO$_2$/g at 80 °C and 981 $\mu$mol SO$_2$/g at 30 °C. The strength (199 kJ/mol) of its strongest basic sites is intermediate to those of alumina and magnesia. When the calcined HT is exposed to steam at 760 °C, the mesoporous house-of-cards structure collapses forming an MgO and Al spinel mixture; the solid's DFT SA is reduced to 87 m$^2$/g from 254 m$^2$/g and loses most of its sorption capacity for SO$_2$. Thus, after recirculating in a fluid cracking unit, any LDH material initially present in FCC compositions will convert to a MgO and Al-spinel mixture; that is, to compounds whose reactivity with sulfur oxides has long been recognized. Microcalorimetry experiments reported in this paper show that the strength of the strongest basic sites is less than 200 kJ/mol. Sulfite formation is exothermic ($\Delta$H of ((MgSO$_3$) = -1009.6 kJ/mol) and it is unlikely that the aforementioned initial heats are related to this compound generation.

To elucidate the porous structure of layered materials a method based on molecular scale statistical thermodynamics is needed. The DFT provides such a method, and allows us to extract from adsorption data a much more complete description of the porous structure of a material than traditional methods. In general, traditional methods of nitrogen porosimetry data representation yield surface area values that differ from actual areas in a manner that depends on the solid's pore structure, and when pore widths approach molecular dimensions the differences can be very large. Only in the case of solids that do not contain significant amounts of micropores, such as the solid studied in this paper, do DFT methods yield surface area values that do not markedly deviate from Langmuir, BET, and BJH results.

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