Strontium(II) chabazite-type silicoaluminophosphate prepared via microwave synthesis and partial detemplation: A superior CO$_2$ adsorbent

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A B S T R A C T

A silicoaluminophosphate with a chabazite-type framework (SAPO-34) was synthesized via a microwave heating assisted hydrothermal method. The effect of variables such as crystallization time and aging time on the microwave-assisted synthesis was investigated in detail. X-ray diffraction (XRD), scanning electron microscopy (SEM), inductively coupled plasma mass spectrometry (ICP-MS), solid-state magic angle spinning nuclear magnetic resonance (MAS NMR) measurements, porosimetry and pure component CO$_2$ gas adsorption were used to characterize the materials structural and textual properties. High purity and small size cubic crystals (0.2–1 μm) of Na-SAPO-34 with large surface area were successfully synthesized by microwave heating after 42 h, compared to 8 days required via the conventional method. It has been discovered that a short aging time of 8 h favors formation of small crystals, plausibly due to an enhanced nucleation. In addition, MAS NMR spectra showed that framework silicon atoms are present mainly as Si(4Al), which evidences a framework with minimal amount of faults. As-synthesized materials were ion exchanged with Sr$^{2+}$ after partial detemplation and afterwards tested for CO$_2$ uptake at room temperature. Elemental analyses revealed superior Sr$^{2+}$ loadings per unit cell, probably due to the neat crystalline characteristics. As a result, the materials also exhibited superior CO$_2$ adsorption capacities, particularly at low partial pressures where the sorbent–sorbate interactions are predominant.

1. Introduction

Silicoaluminophosphate (SAPO) molecular sieves have been widely studied for catalysis, adsorption and other important applications [1–11]. In particular, SAPO-34, a chabazite (CHA) type framework, has been successfully used to separate carbon dioxide from different gases via physical adsorption [6,12,13]. It has been reported recently that alkaline-earth metal ion-exchanged SAPO-34 materials could be promising adsorbents for the selective removal of CO$_2$ at temperatures and pressures that approach ambient conditions [5,6,14,15]. Furthermore, Hernández-Maldonado and co-workers have shown that increasing Sr$^{2+}$ extra-framework cation loadings onto SAPO-34 improves its adsorptive capacity for CO$_2$ at low partial pressures [14,15], particularly after employing partial detemplation of the as-synthesized SAPO-34 materials [15]. Partial detemplation consists of elimination of fragments of the structure-directing agent (SDA) employed during the synthesis to avoid the formation of acid sites that arise from an otherwise complete Hoffmann-type degradation. These acid sites usually occupy cation sites in the SAPO-34 framework that are forbidden to divalent cations such as strontium(II), limiting the ion exchange and adsorption capacity [15]. Other factors that may limit the textual and adsorption properties of SAPO-34 frameworks include the presence of crystal faults, but one possible way of overcoming this is via microwave-assisted synthesis.

It has been discovered that synthesis of zeolites via microwave-assisted heating has several advantages over conventional heating, such as fast crystallization, phase selectivity, narrow particle size distribution, abundant nucleation, morphology and size control and rapid and heating [13,16–19]. Microwave-assisted synthesis has been widely used in the synthesis of different zeolitic materials [18,20–25] and recently extended to the preparation of SAPO frameworks [13,16,17,26]. For instance, it has been reported that nanosized SAPO-34 crystals (100–500 nm) can be synthesized from colloidal solutions and in the presence of tetraethylammonium hydroxide (TEAOH) as a template [17]. In addition, H$^+$–SAPO-34 zeolites displaying ~0.5 μm crystal size with a narrow particle size distribution and preferential adsorption of CO$_2$ over that of CH$_4$ have been prepared via phase transformation of SAPO-5 under microwave-assisted heating [13]. Although these accounts are the first reports of successful synthesis of SAPO-34 via the microwave route, they do not include analyses of ion-exchange properties and how this may enhance adsorption of gases. Slangen et al.
have reported that a large number of nuclei would result in small crystals of zeolite which can be advantageous in ion-exchange [27].

The main objective of the present work is to study microwave-assisted heating and subsequent partial detemplation to enhance ion exchange of strontium onto SAPO-34 and the effect of these on the material CO2 physical adsorption performance, particularly at low partial pressures. Removal of traces of CO2 from light gas mixtures is still a major challenge, particularly in closed system applications where regeneration is limited by availability of energy resources.

2. Experimental

2.1. Microwave-assisted and conventional hydrothermal synthesis of Na-SAPO-34

Na-SAPO-34 molecular sieves were synthesized by using microwave and conventional heating methods, respectively. The synthesis gel was prepared by first adding aluminum isoproxide (Aldrich) to o-phosphoric acid (85 wt.%, Sigma–Aldrich) under well mixing conditions. A colloidal silica solution (30 wt.% SiO2 LUDOX AM-30, Sigma–Aldrich) and sodium hydroxide (Sigma) were then added to the aforementioned mixture and mixed for 1 h. The structure directing agent (SDA), tetraethylammonium hydroxide (TEA-OH, Fluka), was added dropwise and the final mixture allowed to age for a specific amount of time. Table 1 summarizes all the reaction conditions. The elemental composition of the final gel mixture in molar oxide ratios was 0.5(TEA)2O:0.3 Na2O:1.3 Al2O3:0.6 SiO2:P2O5:60 H2O. Microwave-assisted hydrothermal syntheses under autogenous conditions were carried out using 100 ml Teflon vessels (XP-1500 Plus, CEM Corporation) and a microwave oven (MARS-5, CEM Corporation). The super-saturated gels were heated to a temperature of 180 °C at a rate of 20 °C/min and under a power input that did not exceed 400 W. To avoid damaging of the optical fiber temperature probe and its sapphire thermowell, it was placed into a reference vessel containing a gel mixture of similar composition as the one described before but neutralized to pH ~7 using hydrochloric acid (1 M). For conventional hydrothermal crystallization, the gel was loaded into Teflon lined auto claves and heated in a forced-convection oven to 180 °C. Recovery of the solids in all cases was accomplished after allowing the vessels to reach room temperature followed by centrifugation. Powders were dried overnight at 60 °C also using forced convection ovens.

2.2. Detemplation and ion exchange

Treatment of as-synthesized Na-SAPO-34 at high temperature to remove the TEA+ cations from the porous material framework was carried out by using a two-step thermal method previously reported by Hernandez-Maldonado and co-workers [15]. The samples were placed inside quartz cylindrical reactors designed to fit inside the tubular chamber of a computer-controlled muffle furnace and under an air flow of 100 cm3/min. The gas was pre-treated with moisture and hydrocarbon traps to ensure purity. During the two-step thermal treatment method, the sample was first calcined in air for 15 h at a temperature of 430 °C for partial detemplation. The resulting sample was then ion exchanged with Sr2+ as described below and afterwards calcined in air at a rate of 15 °C/min and maintained at 500 °C for 15 h. This last stage calcination step is crucial to remove any tenacious SDA residues.

The ion exchange was performed in a one-step equilibration batch system using a high cation chloride salt/zeolite aqueous solution with a molar ratio of 20:1. The exchange was performed under vigorous stirring at 60 °C for 24 h. Further details on the methods and procedures can be found elsewhere [5,14].

2.3. Materials characterization

2.3.1. Scanning electron microscopy (SEM), X-ray powder diffraction (XRD), and inductively coupled plasma mass spectrometry (ICP-MS)

SEM micrographs were obtained using a JEOL JSM-6390 instrument fitted with a SEI detector and operating at a voltage range of 5.0–20.0 kV. The SEM micrographs were employed to identify the morphology and estimate the crystal size of SAPO-34 samples prepared by microwave, conventional heating methods and for Sr2+ ion exchanged samples.

XRD patterns of the as-synthesized Na-SAPO-34 materials prepared via microwave-assisted and conventional heating methods were obtained using a Rigaku ULTIMA III X-ray diffraction unit fitted with cross beam optics and a Cu Kα target operating at 40 kV and 44 mA. Patterns were gathered for 2θ diffraction angles ranging from 1° to 70° at a scanning rate of 0.02°/s. The patterns were used to corroborate the phase of the as-synthesized materials prepared by the different methods and to perform unit cell indexing using the CRYSFIRE software suite and the TREOR-90 indexing routine [28,29].

Compositional data of the unit cell of the detemplated and the ion-exchanged SAPO-34 materials were estimated via inductively coupled plasma mass spectrometry (ICP-MS) analysis (Agilent 7500ce).

2.3.2. Textural properties and CO2 adsorption equilibrium isotherms

Surface area and pore volume were estimated for Na-SAPO-34 samples prepared via microwave-assisted and conventional heating methods (see Table 1) after degassing at 375 °C. The textural properties were calculated after evaluation of N2 volumetric equilibrium adsorption isotherm data gathered at ~196 °C using a Micromeritics ASAP 2020 instrument outfitted with turbo molecular drag pumps. It should be mentioned that the SAPO-34 particles external surface area was estimated by means of a t-plot analysis. Details about this method are available elsewhere [30].

Carbon dioxide equilibrium isotherm data for detemplated Na-SAPO-34 and ion exchanged Sr-SAPO-34 samples were obtained at room temperature also using the Micromeritics ASAP 2020 instrument. Gases used were CO2 (Ultra High Purity Grade, Praxair), and helium (High Purity Grade, Linde). Helium was used as a backfill gas after the adsorbent degassing stage and removed via ultra-high vacuum prior to adsorption tests. All samples were pre-treated in vacuum at 375 °C to remove water molecules strongly bound to the structure.

2.3.3. Solid-state magic angle spinning nuclear magnetic resonance (MAS NMR)

Solid-state 27Al and 29Si magic angle spinning nuclear magnetic resonance (MAS NMR) measurements were performed on an ultranarrow bore 19.6 T magnet with a Bruker DRX NMR console where the 27Al and 29Si Larmor frequencies are 217.14 and 165.55 MHz, respectively, using an in-house made single resonance 4 mm MAS
NMR probe. The samples were spun at 8 kHz. The $^{31}$P solid-state MAS NMR measurements were carried out on a Bruker DMX 300 MHz NMR spectrometer where the $^{31}$P Larmor frequency is 121.52 MHz. A 4 mm Bruker MAS NMR probe was used with a sample spinning rate of 12 kHz for all $^{31}$P measurements. For the $^{27}$Al analyses, the chemical shifts were referenced to a saturated Al$_2$(SO$_4$)$_3$ solution. Two hundred and fifty six transients were used to record the $^{27}$Al NMR spectra with a recycle delay of 1s, pulse length of 1.0 μs (∼10° flip angle), and 1024 FID points with 5 μs dwell time. For $^{29}$Si, the chemical shifts were referenced to 4,4-dimethyl-4-silapentanesulfonate sodium (DSS). Five hundred and twelve transients were used to accumulate the $^{29}$Si signals with a recycle delay of 10 s, pulse length of 2 μs (∼15° flip angle), and 800 FID points with 10 μs dwell time. For $^{31}$P, the chemical shifts were referenced to a saturated Na$_2$HPO$_4$ solution. The NMR experimental parameters were: 256 transients, 5 s recycle delay, 1.5 μs pulse length (∼10° flip angle), and 1536 FID points with 5 μs dwell time.

3. Results and discussion

3.1. Microwave synthesis characterization

Several samples were synthesized via microwave irradiation at 180 °C and different reaction and aging times. A non-crystalline phase was detected after 24 h while a SAPO-34 phase was

![Fig. 1. XRD profile of the as-synthesized Na-SAPO-34 samples prepared by different methods. Refer to Table 1 for sample descriptions.](image1)

![Fig. 2. SEM images of Na-SAPO-34 prepared by microwave-assisted heating at 180 °C for 36 h and different aging times: (A) 8 h, (B) 16 h and (C) 24 h. SEM image for sample prepared at 180 °C for 42 h and an aging time of 8 h is shown in (D).](image2)
observed after 42 h as evidenced by XRD and SEM analyses (Figs. 1 and 2, respectively). The XRD patterns for SAPO-34 are in good agreement with those found in the literature [6,8,15,17]. Furthermore, the XRD patterns observed for samples prepared by microwave irradiation and conventional heating method were indexed under the hexagonal system (Table 2), and there are no significant changes in the unit cell dimensions of the samples synthesized by different methods.

SEM images (Figs. 2 and 3) show morphological features that should be discussed in detail. As shown in Fig. 2A, the microwave-assisted hydrothermal synthesis performed for 36 h yielded cubic crystals of ca. 0.2–1 μm in size. However, there were also large amounts of unreacted amorphous material present in the particles population. As the reaction time was increased to 42 h, the cubic crystals of the SAPO-34 phases appeared in size 0.2–1 μm and there were no noticeable presence of unreacted materials.

Aging time has been reported to greatly affect the nucleation process in microwave-assisted synthesis of zeolites [27] and was therefore also studied here. Fig. 2A–C shows SEM micrographs for the particle products of the 36 h synthesis and different aging times. From Fig. 2A, one could see that aging for 8 h resulted in some cubic crystals (0.2–1 μm) but also plenty of unreacted amorphous material. Upon increasing aging time (to 16 h) more cubic crystals were formed but with an average size of 0.5–2 μm (Fig. 2B). After 24 h of aging, the crystal size increases to ca. 2 μm but there is still some minor amorphous phase present (Fig. 2C). Apparently, 36 h of synthesis, independent of the aging time, results in short lived nucleation rates since all samples exhibited the presence of amorphous material. Only when the synthesis mixture is aged for 8 h and treated for 42 h was pure Na-SAPO-34 obtained (Fig. 2D). This sample consists of small crystals with size in the 0.2–1 μm range, which is similar to the results obtained for 36 h synthesis and employing the same aging time. As aging time is increased to 16–24 h, the particle size distribution is in the range of 0.2–2 μm. Myatt et al. reported that the average crystal size strongly depends on the total number of nuclei produced while the breadth of the size distribution correlates with the duration of the nucleation period [31]. Therefore, it is possible to assume that in our case study, some nuclei have been formed during the aging process at room temperature and that longer aging periods would basically increase the crystal size distribution. For a narrow crystal size distribution, it would therefore be favorable to have a short nucleation period of 8 h.

Porosimetry is also an excellent tool to characterize crystal textural properties as well as the presence of amorphous phases. For instance, samples synthesized for 36 h under microwave irradiation and 8 h aging have a relatively small surface area (ca. 117 m² g⁻¹) due to the presence of unreacted amorphous material. Upon an increase in reaction time, the surface area became larger (see Table 1) due to the higher purity of the resulting material. The material obtained after aging for 8 h and microwave-assisted heating for 42 h has the largest surface area (588 m² g⁻¹) and the best cubic crystals with little amorphous phases (Fig. 2D). In addition, a t-plot analysis indicated that the same material had the largest external surface area when compared to the other variants (see Table 1). This should be expected since the presence of smaller crystals should result in an increase in surface area per unit weight.

For a comparison, we also performed the synthesis of Na-SAPO-34 via conventional heating methods and for 36 h, 4 days and 8 days, respectively. Fig. 3 shows how some cubic crystals were formed after 36 h or 4 days of conventional heating. However, there is also plenty amounts of unreacted amorphous material in the product. Upon an increase of the reaction time to 8 days, only minor unreacted amorphous material appeared within the cubic crystals of Na-SAPO-34 (Fig. 3C). However, the average crystal size of Na-SAPO-34 in this case is much larger (up to 5 μm) when compared to the crystals obtained from microwave-assisted heating. In addition, the surface area of the material synthesized via

![Fig. 3. SEM images of Na-SAPO-34 prepared by conventional hydrothermal synthesis at 200 °C for (A) 36 h, (B) 4 days and (C) 8 days.](image_url)

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<th>Table 2</th>
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<td>Estimated unit cell parameters for as-synthesized Na-SAPO-34 samples prepared by microwave and conventional heating hydrothermal synthesis methods.</td>
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<tr>
<td>Sample</td>
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<tr>
<td>Na-SAPO-34 (CH-200-8)</td>
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<tr>
<td>Na-SAPO-34 (MW-180-36-16)</td>
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<tr>
<td>Na-SAPO-34 (MW-180-42-8)</td>
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conventional heating for 8 days is smaller than the one prepared via microwave (see Table 1). This demonstrates that the microwave method not only saved the time for synthesis of Na-SAPO-34, but also improved the quality of the textural properties.

3.2. Coordination environment

MAS NMR was employed to study the environment of Al, Si, and P tetrahedra in SAPO-34 materials prepared by microwave heating and different conditions. Fig. 4 collects the $^{27}\text{Al}$, $^{29}\text{Si}$, and $^{31}\text{P}$ MAS-NMR spectra for all the variants, including the as-synthesized material, partially detemplated Na-SAPO-34 and ion-exchanged Sr-SAPO-34 samples. For all the materials, $^{27}\text{Al}$ NMR spectra show four peaks at around 80, 40, 12 and $-10$ ppm, which is similar to the results previously reported by our group for Na-SAPO-34 prepared via the conventional method [14]. The strong resonance peak at around 40 ppm corresponds to aluminum centers in a tetrahedral environment. Meanwhile, the small peak at 12 ppm may be due to aluminum with penta or hexa-coordination states. Another small peak shown at around 80 ppm is probably due to resonance contributions from other tetrahedral aluminum families [14,32]. For the $^{27}\text{Al}$ peak at approximately $-10$ ppm, the resonance should be attributed to octahedral aluminum species probably resulting from thermal treatment to remove the TEAOH [32]. For as-synthesized Na-SAPO-34 prepared via microwave irradiation for 36 h, the intensity of this peak decreased slightly after ion-exchange with Sr$^{2+}$, but still remains higher when compared to the intensity of the peak in Na-SAPO-34 prepared after 42 h. This indicates that the Al centers in the latter sample contain less octahedral environments and may explain its higher purity.

The $^{31}\text{P}$ NMR MAS spectrum of Na-SAPO-34 (MW-180-36) shows four distinct resonances (−11.9, −16.2, −20, and −30.3 ppm). For the high resonance peak at −30.3 ppm, the coordination environment should be attributed to the phosphorous atoms bounded to four aluminum atoms $\text{P(OAl)}_4$ [33]. Meanwhile, the three remaining weak resonances could be related to three non-equivalent P sites [32]. After partial detemplation at 430°C (i.e., Na-SAPO-34 MW-180-36-PD), the intensity of the peaks at −11.9 and −16.2 ppm decreased, eventually disappearing after completion of the ion-exchange and high temperature calcination at 500°C (i.e., Sr-SAPO-34 (MW-180-36-16)). Therefore, one may conclude that the two peaks at −11.9 and −16.2 ppm might be related to the coordination of phosphorous with the SDA, while the peak at −20 ppm should be attributed to phosphorous probably coordinated to water molecules. It is interesting to note that the Na-SAPO-34 (MW180-42) sample exhibit broadened resonances at −11.9 and −16.2 ppm while the resonance at −30.3 ppm shifted to −29.5 ppm. However, the intensity of these peaks is much lower than that of Na-SAPO-34 (MW-180-36), probably indicating that the previously discussed scenario correspond to phosphorous atoms coordinated with the SDA cation in the amorphous phases.

$^{29}\text{Si}$ NMR spectra are also presented in Fig. 4. All the SAPO-34 samples showed a peak at −90 ppm, which should be assigned to Si(4Al) [3,32,33]. It is interesting to note that the linewidth of the resonance at −90 ppm for the samples Sr-SAPO-34 (MW-180-36-16), Na-SAPO-34 (MW-180-36-16-PD), and Na-SAPO-34 (MW-180-42-8-PD) is about half when compared to the one observed for the other as-synthesized samples, which seems to inversely correlate with the linewidth of $^{27}\text{Al}$ at 40 ppm and $^{31}\text{P}$ at $\sim$−29.5 ppm. This is probably due to effects from the detemplation process. Comparing the spectra of the as-synthesized samples, the

![Fig. 4. $^{27}\text{Al}$, $^{29}\text{Si}$, and $^{31}\text{P}$ MAS-NMR spectra of SAPO-34 materials. Please refer to Tables 1 and 3 for sample descriptions.](image-url)
sample prepared after 36 h of reaction shows a broadening in the
–100 to –120 ppm range, which should be attributed to a small
amount of unreacted silica [32]. It should be mentioned that
Na-SAPO-34 samples prepared by the conventional thermal meth-
ods also exhibit this broadening [14]. However, Na-SAPO-34
(MW180-42) does not show the peak broadening, which indicates
that its framework silicon atoms are present mainly as Si(4Al) and
evidences the presence of a framework with minimal amount of
faults.

3.3. Ion exchange with strontium and CO$_2$ adsorption performance

Na-SAPO-34 materials prepared via microwave-assisted and
conventional heating were also ion exchanged with Sr$^{2+}$ and tested
for CO$_2$ adsorption. A thorough explanation of the underlying
adsorption mechanism is available elsewhere and therefore would
be omitted here [5,6]. Fig. 5 shows data for CO$_2$ equilibrium
adsorption for all the SAPO-34 sorbent materials at 25 °C. Sr-
SAPO-34 materials prepared using microwave irradiation at

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**Table 3**

<table>
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<tr>
<th>Sample description</th>
<th>Product</th>
<th>Unit cell</th>
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<tr>
<td>Microwave synthesis at 180 °C for 42 h. Aging for 8 h. Material detemplated at 500 °C</td>
<td>Na$<em>{1.54}$H$</em>{3.45}$[Si$<em>{4.33}$Al$</em>{18.33}$P$<em>{13.34}$O$</em>{72}$]·xH$_2$O</td>
<td></td>
</tr>
<tr>
<td>Microwave synthesis at 180 °C for 42 h. Aging for 8 h. Material partially detemplated at 430 °C, followed by ion exchange with Sr$^{2+}$ and calcination at 500 °C</td>
<td>Sr-SAPO-34 (MW-180-42-8-PD)</td>
<td>Na$<em>{0.25}$H$</em>{0.11}$Sr$<em>{1.86}$[Si$</em>{3.86}$Al$<em>{18.11}$P$</em>{14.03}$O$_{72}$]·xH$_2$O</td>
</tr>
<tr>
<td>Microwave synthesis at 180 °C for 36 h. Aging for 16 h. Material partially detemplated at 430 °C, followed by ion exchange with Sr$^{2+}$ and calcination at 500 °C</td>
<td>Sr-SAPO-34 (MW-180-36-16-PD)</td>
<td>Na$<em>{1.01}$H$</em>{0.60}$Sr$<em>{1.25}$[Si$</em>{4.30}$Al$<em>{17.91}$P$</em>{13.79}$O$_{72}$]·xH$_2$O</td>
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*Note: The amount of H$_2$O per unit cell (x) is ca. 6–7 according to the TGA results [15].*
180 °C and 42 h (MW-180-42) adsorbed ca. 1 mmol of CO₂ per gram of solid at the lower measured partial pressure. This uptake amount is approximately twice as that observed for Sr-SAPO-34 prepared by the conventional heating method and even the one for Sr-SAPO-34 synthesized for 36 h also via microwave heating. This increase in CO₂ uptake capacity correlates well with the amount of Sr²⁺ per unit cell reported in Table 3 and indicates that it appears that the crystal size of Na-SAPO-34 plays an important role in the exchange of Sr²⁺ ions into the unit cell. This evidently will affect the CO₂ adsorption performance as well.

### 4. Conclusions

High purity Na-SAPO-34 was successfully synthesized by combining aging and microwave-assisted heating methods. Short aging times were found to favor the formation of small crystals and a narrow size distribution. Synthesis at 180 °C for 42 h resulted in materials with outstanding textural properties. Furthermore, MAS NMR spectra revealed that this approach results in structures with less faulting when compared to those obtained via conventional thermal methods. Meanwhile, careful elemental analyses after ion exchange of partially detemplated as-synthesized materials revealed superior strontium(II) loadings. This at the same time resulted in a considerable increase in CO₂ adsorption, particularly at low partial pressures.

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