Synthesis, Characterization and Mild Detemplation of Novel Cobalt Rich SBE Type Nanoporous Materials

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ABSTRACT

The optimization of the synthesis, extended characterization and evaluation of the adsorption properties of cobalt-rich SBE type aluminophosphates (CoAPO-SBE) were investigated. According to X-ray diffraction (XRD), scanning electron microscopy (SEM) and porosimetry analyses, a longer gel aging time results in crystals with less faulting. We employed a vacuum assisted thermal process to avoid destruction of the periodic framework, since the porous properties of the framework could only be evaluated upon removal of the structuredirecting agent (SDA) species (i.e., detemplation); this approach resulted in micropore surface areas of ca. 600 m²/g. Coupled thermal gravimetric and Fourier transformed infrared spectroscopy (TGA/FTIR) analyses suggested that the decomposition of the SDA takes place in a multi-step fashion, with products that included ammonia, carbon monoxide, carbon dioxide and water. In situ high temperature XRD tests indicated that the detemplated open framework is also highly unstable to oxidative and high temperature conditions probably due to the large content of transition metal centers (Co/Al ~ 1). Attempted detemplation of CoAPO-SBE materials by UVozone followed by vacuum assisted thermal process was also performed. The complete process itself appears to be more efficient and less harmful to the SBE framework, but will require further investigation. We found, however, that it is possible to effectively functionalize these materials using coupled vacuum assisted partial detemplation and solid-state ion exchange (PD/SSIE) at mild temperatures. CoAPO-SBE was detemplated and Na⁺ or Li⁺ species were introduced by SSIE in an attempt to modify its surface properties while preserving the framework's structural and textural properties. The resulting porous materials were also tested for equilibrium adsorption of CO₂. The best CO₂ loading capacities were observed in the sodium-SBE variants at 25 °C for both low and high partial pressure ranges. Furthermore, this adsorbent material exhibited good selectivity toward CO₂ over CH₄ or N₂. Structural refinement of the CoAPO-SBE before and after CO₂ adsorption process was also explored.

RESUMEN

La optimización de la síntesis del aluminofosfato rico en cobalto tipo SBE (CoAPO-SBE), su amplia caracterización y evaluación de sus propiedades de adsorción fueron investigadas. De acuerdo al análisis de difracción de rayos-X (XRD), microscopia de barrido electrónico (SEM) y de porosimetría, a mayor tiempo de añejamiento del gel, resulta en cristales con menos fallas. Se empleó un proceso termal asistido al vacío para remover el agente director de estructura (SDA) ó plantilla y así evitar la destrucción de la periodicidad de la estructura, ya que las propiedades porosas de la estructura SBE pueden ser evaluadas una vez se remueve la plantilla; esta aproximación resultó en áreas de superficie microporosas cerca de 600 m²/g. Análisis termogravimétrico, acoplado a espectroscopia infrarroja con transformada de Fourier (TGA/FTIR), sugirieron que la descomposición de la plantilla tiene lugar en una serie de etapas con productos que incluyen amoniaco, monóxido de carbono, dióxido de carbono y agua. Difracción de rayos-X in situ a altas temperaturas indicó que la estructura sin plantilla es altamente inestable a condiciones oxidativas y a altas temperaturas, esto probablemente es debido a la alta concentración de centros tetraédricos del metal de transición (Co/Al ~1). Se intentó la remoción de plantilla de materiales de CoAPO-SBE mediante tratamiento con luz ultravioleta (UV) y ozono, seguido del proceso termal bajo vacío. El proceso completo aparenta ser más eficiente y menos dañino a la estructura de SBE y requiere investigación adicional. Sin embargo, se encontró que es posible funcionalizar eficientemente estos materiales usando la técnica de remoción parcial de plantilla acoplada con intercambio iónico en fase solida (PD/SSIE) a temperaturas moderadas. La estructura de CoAPO-SBE, una vez removida la plantilla, fue intercambiada con especies de Na⁺ o Li⁺ por SSIE, en un intento por modificar las propiedades de su superficie mientras se preservan las propiedades estructurales y texturales de SBE. Los materiales porosos resultantes fueron también probados para adsorción en el equilibrio de CO₂. La mejor capacidad de adsorción de CO₂ fue observada en la variante de SBE con sodio a 25 °C a altos y bajos rangos de presión. Además, este material adsorbente exhibió buena

selectividad por CO₂ sobre nitrógeno y metano. Refinamiento estructural del material CoAPO-SBE antes y después del proceso de adsorción de CO₂ fue también explorado. To my family . . .

Fidi, Bancho and Mila...for all the confidence, support and love they always give me, which makes me a better human being.

Edwin and Matias...for making my life meaningful, I love you.

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Chapter 1 Introduction

1.1 Nanoporous Materials

In general, nanoporous materials refer to materials that contain pores that are less than 100 nm in diameter [1, 2]. This feature provides a large surface to volume ratio and a highly ordered, uniform pore structure [3], characteristics that could potentially impact many applications including microelectronics, pharmaceutical, clean energy development, and environmental, just to mention a few. For example, the petroleum industry has employed naturally occurring nanoporous materials as catalysts (i.e., aluminosilicates) for decades now. However, the majority of the catalysts and adsorbents used today by this and other industrial sectors are synthetic forms and polymorphs. Such milestone has also provided the much-needed control over the catalysts properties, including dispersion and loading properties. In addition, the scaling up of synthetic nanoporous sorbent synthesis has provided numerous opportunities to develop advanced separation membranes, including those designed for gas applications such as the removal of SO₂, NO_x and treatment for VOCs emissions [4]. All these particular membrane applications rely on the nanoporous materials size-exclusion principles as well as surface functionality. For the former, the pore size range of the materials

has to fall in the microporous region (according to the IUPAC definition for porous materials).

Crystalline microporous materials are solids that contain interconnected cavities or channels with pores of molecular dimensions typically in the 3 to 20 Å range [5, 6]. Hydrothermal recipes used for the preparation of microporous solids include the use of an organic amine molecule. The role of the organic part in the synthesis is threefold: templating, structure-directing agent (SDA) and/or space filling. During the synthesis of porous solids, irrespective of what is the role of the amine molecules, these species are located within the cavities or channels and appear to be one of the key variables to direct the formation of a particular structure [6, 7]. But the release of the framework porous properties can only be achieved after removal of the SDA species (detemplation). These are usually eliminated from the voids using high temperature atmospheres to break down and desorb the template via Hoffman elimination [8-10]. Still, the challenge today is to minimize the impact of the detemplation process on the nanoporous framework integrity, especially in cases where the materials are made of large concentrations of transition metals [11]. This family of materials includes metal substituted aluminophosphates (M^{n+} AlPOs; M = Co, Mn, Fe, Ti, Cr...).

Considerable research work for the development of ultra-large pore structures has produced materials like VPI-5 and AlPO4-8, which have pore windows of 18- and 14member rings, respectively [12-14]. However, these materials also have frameworks with channels with the largest pore in only one dimension and do not have extra framework metal cations because their net structural charge is neutral. Recent studies indicate that the great challenge faced by the nanoporous materials scientific community is how to successfully scale-up laboratory studies for industrial level applications. Although the potential applications of such materials have been widely studied in many areas, more efforts are still needed for the continuing study of their practical applications to commercialize nanoporous materials in the near future [15, 16]. The following sub-sections are intended to briefly summarize the work that has been reported so far for nanoporous AlPOs and metal-substituted AlPOs.

1.2 Isomorphous Substitution of Cobalt into AIPO Frameworks and Some Applications

The Al/P ratio in AlPO frameworks usually approaches unity, making the framework electrostatically neutral, with no active sites present as in the case of a pure siliceous zeolite (SiO_2) [6, 17]. Opposite to siliceous zeolites that are hydrophobic, almost all the AlPO materials with Al/P = 1 are somewhat hydrophilic, suggesting that the framework species in an AlPO has affinity to polar molecules [18]. The isomorphous substitution of framework aluminum atoms with divalent transition metals, such as Mn, Co, Fe, etc., generates negative framework sites and makes these microporous materials very successful selective catalysts [19]. Choudary and co-workers, who worked on cobalt substituted aluminophosphate molecular sieves prepared under microwave-hydrothermal conditions at 180 °C, were among

the first to demonstrate the possibility of successful crystallization of SSZ-51 frameworks with Co/Al ratios of 0.1 [20].

Cobalt containing porous materials are important selective oxidation catalysts in, for example, liquid phase oxidation of alkanes with dioxygen and selective oxidation of cyclohexane to cychlohexanone [21]. Selvam and Mohapatra have developed a Co-HMA catalyst that exhibits excellent activity for the oxidation of cycloalkanes under mild reaction conditions. Co-HMA, however, does not show removal or segregation of framework cobalt [22], perhaps due to the low Co/Al ratio. Their work also included HMA type AlPOs with a maximum Co/Al ratio of 0.053. It should be mentioned that there also exists a correlation between cobalt framework substitution and acidity. This has been investigated during the development of solid acid catalysts for methanol conversion to light olefins [17].

1.3 Cobalt Rich 3D Microporous Aluminophosphate: CoAPO-SBE

During the late 1990s, Stucky and co-workers reported a group of novel AlPO frameworks with a Co/Al ratio between 0.6 and 1.0 [23]. Recently, Hernández-Maldonado and co-workers developed a powder form of a cobalt-rich AlPO having a ratio of Co/Al \sim 0.85 and (Co+Al)/P > 0.9 [11].

Crystals of Co-SBE are typically grown as hexagonal plates with a characteristic length of about 100 μ m. These materials consist of an orthogonal channel system with 12-ring apertures in two dimensions and 8-ring apertures in the third (Figure 1.1a). Each of the resulting interconnected supercages measures 20 Å by 20 Å by 15 Å (Figure 1.1b), which

correlates to a theoretical surface area of ca. 1100 m²/g. For a 12-ring tetrahedral atom ring such an amount of available surface area is impressive, exceeding the capacity of traditional Faujasite zeolites by more than 20%. Faujasites comprise most of the catalysts and adsorbents used in petrochemical and gas processing industries [2, 24]. It should be mentioned that the cobalt aluminophosphate system is also attractive because the incorporation of small amounts of transition metals into zeolitic frameworks influences their properties and generates their redox activity [19]. Transition metal-modified nanoporous materials with aluminophosphate frameworks are already reported to be good catalysts for acid-catalyzed reactions and oxidations, hydroxylation and polymerization reactions [15, 16].



Figure 1.1 SBE (A) framework and (B) supercage. Source: International Zeolite Association [25].

Hernández-Maldonado and co-workers have used solvent extraction and ion exchange techniques for the removal of the SDA agent from a thermally unstable cobalt substituted aluminophosphate. However, treatment in both oxidative and vacuum atmospheres was also assessed to understand the principles of the SDA (1,9-diaminononane) decomposition and interaction with the framework [11]. The calcination process in oxygen-only atmospheres showed that even partial removal of SDA resulted in considerable faults and distortion of the SBE framework. Treatment using vacuum, on the other hand, resulted in a material with a surface area and super cage diameter of ca. 320 m²/g and 9 Å, respectively [11]. But the attained surface area was still below the target theoretical value and much work was needed to understand the SDA interaction within the framework and how to remove it completely without compromising the material structural integrity. Therefore, one of the challenges of the present work is the development of alternatives for detemplation techniques based on the nature of the SDA interaction with the SBE framework.

1.4 Overview of the Dissertation

The principal objective of this work is the development of non-traditional detemplation techniques to produce a novel nanoporous SBE type aluminophosphate material for adsorption applications. Three different strategies to produce this novel material were implemented; the first one being the optimization of the material synthesis and extended characterization, the second one consisting in the evaluation of the structural stability of the detemplated materials in presence of water. The third one, the incorporation of alkali metals

to produce a porous M^+ -CoAPO-SBE (M = Na or Li) adsorbent via couple partial detemplation and solid-state ion exchange (PD/SSIE).

Chapter 2 presents the effect of the hydrothermal synthesis time on the long-range structural properties, textural properties and morphology of cobalt aluminophosphate materials CoAPO-SBE. We also present the mechanism of decomposition of the organic template in CoAPO-SBE. Finally, we present information about the structural stability of the detemplated materials in the presence of water. This part of the work was published in the Journal of Material Science (Springer) in 2012.

Chapter 3 focuses on the study of different strategies for mild detemplation of CoAPO-SBE. In this chapter we explore a couple of alternative treatments for the removal of the SDA from the CoAPO-SBE, like cleavage reactions, to break amine C-N and/or C-C bonds and UV/ozone treatment.

In Chapter 4, we present the use of a partial detemplation and solid-state ion exchange (PD/SSIE) strategy at mild temperatures to produce a porous CoAPO-SBE adsorbent with extraframework metal species. Also, the CoAPO-SBE modified materials were tested for adsorption of CO_2 , CH_4 and N_2 to elucidate the level of selectivity. The work presented in this chapter was published in the Journal of Microporous and Mesoporous Materials (Elsevier Inc.) in 2012.

Chapter 5 focuses on the exploration of structural refinement of CoAPO-SBE before and after CO₂ adsorption process. The work presented in this chapter, and also the FTIR analyses discussed in Chapter 4, were conducted during the internship at the University of Turabo as part of the PhD degree requirement of the UPRM Chemistry Department. Finally, a summary of the more relevant contributions of this dissertation work is presented in Chapter 6. Complementary data and additional experiments are also included in an Appendix Section.

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Chapter 2

SBE type cobalt-aluminophosphates (Co/Al~1): Synthesis aging effect, detemplation mechanism from coupled TGA/FTIR analyses and structural stability after detemplation

Cobalt-rich SBE-type aluminophosphate microporous solids were prepared by employing different aging periods during the hydrothermal synthesis. According to XRD, SEM and porosimetry tests, aging for 168 hours results in a material with good long-range framework and textural features. The latter were analyzed after careful removal of the structure directing agent (SDA) or detemplation, which produced a micropore surface area of ca. 600 m²/g, the highest ever reported for an aluminophosphate having a multi-dimensional pore system and the highest cobalt-to-aluminum framework ratio. Coupled TGA/FTIR was employed in an attempt to elucidate the SDA decomposition mechanism in both inert and oxidative environments. Careful analysis confirmed that the latter case results in encapsulation of some of the detemplation species due to structural collapsing. Finally, the structural stability of detemplated material was

evaluated in the presence of humidity and ambient air. The results indicate that the framework cobalt appears to readily oxidize upon adsorption of di-oxygen at ambient conditions, leading to an irreversible collapsing of the structure. However, the detemplated microporous solid appears to be stable in the presence of moist inert atmospheres.

2.1 Introduction

The present chapter focuses on the effect of the hydrothermal synthesis time on the morphology, structure and porosimetry of SBE type cobalt aluminophosphate materials and seeks to elucidate a mechanism of decomposition of the organic template via coupled thermal gravimetric/ Fourier transformed infrared spectroscopy (TGA/FTIR) analyses. Vacuum assisted detemplation was employed to generate the porosimetry data since such approach has been proven effective in preserving most of the framework integrity. In addition, the TGA/FTIR data was compared to *in situ* differential scanning calorimetry X-ray diffraction (DSC/XRD) data previously reported by Belen-Cordero and Hernandez-Maldonado for inert and oxidative detemplation. Finally, information about the structural stability of the detemplated materials in presence of water is presented.

2.2 Previous Work

According to single crystal studies reported about a decade ago, SBE type metal substituted AIPO materials have achieved a metal-to-aluminum ratio close to unity [1]. The material known as UCSB-8 was originally obtained in single crystal form, but recently

Hernández-Maldonado and co-workers devised a recipe to produce a single-phase powder form of the cobalt-rich variant [2]

During synthesis, the two governing processes are nucleation and crystal growth [3, 4], the former being critical during the initial stage [3]. In addition, there are parameters of the synthesis that influence the final particle size of materials such as: rate of gel dissolution, number and distribution of nuclei in the gel, crystal growth rate [3], temperature and stirring rate [5] and, last but not least, aging [4, 6]. The literature reports, for instance, that increasing aging time leads to greater dispersion of particles and reduction in crystal size [3, 7-9] and that this could be a result of relative loss energy in the nucleation stage when compared to the crystal energy growth [3]. Another important aspect of the hydrothermal synthesis of microporous crystalline solids is the use of organic amine molecules. Elimination of these organic molecules is achieved using high temperature. This must be performed carefully to avoid damaging the inorganic framework [10] from the accumulation of pressure gradients within the pores, particularly in cases where the materials framework contains a large concentration of transition metals (i.e., $M^{n+}/Al > 0.5$) [11].

One possible way of achieving the maximum transition metal loading (i.e., $M^{n+}/Al \sim 1$) is by employing linear diamines SDAs, as demonstrated by Stucky and co-workers for the synthesis of SBE type single crystal metal substituted AlPOs. It was found that the use of linear amines not only resulted in the maximum inclusion of transition metals but also the formation of AlPO frameworks with multi-dimensional channel systems. In addition, highly metal substituted aluminophosphate systems are attractive because of the incorporation of considerable amounts of transition metal should generate enhanced redox activity [12] as well as catalysts for acidcatalyzed reactions and oxidations, hydroxylation and polymerization reactions [13, 14]. Work performed by Hernández-Maldonado and co-workers focused on the modification of the original synthesis procedure to produce pure phase powders and on the characterization of cobalt-rich SBE. In addition, they extended the study to the preparation of Mn- and Mg-variants in order to understand the process of detemplation in this framework [15].

The morphology of Mg-SBE and Mn-SBE materials differs considerably from that of Co-SBE, plausibly indicating that the transition metal played a role in defining the ultimate materials morphology. Meanwhile, porosimetry analyses indicated that the removal of the SDA from the Co-SBE under vacuum resulted in surface areas in the order of 500 m^2/g , 95% of this value corresponding to a contribution from microporosity [15]. However, the resulting surface area for a detemplated Mn-SBE variant was in order of 100 m²/g, probably as a result of the strong interaction of the protonated SDA with the manganese centers. In fact, magic angle spinning nuclear magnetic resonance (MAS-NMR) spectroscopy analyses evidenced the formation of manganese species with multiple coordination states upon detemplation of the SBE framework, which correlates extremely well with the aforementioned low surface area [15]. In terms of calcination of the SDA in an oxygen-rich atmosphere, even partial removal of SDA could result in considerable faults and distortion in the SBE framework, with surface areas in the single digit [15]. Despite the advances summarized above, much work still remains to be performed in order to fully understand the SDA interaction with the framework and how to remove the template completely without compromising the material structural integrity. Furthermore, it is of utmost necessity to elucidate the stability of the detemplated SBE materials, including tolerance to humid environments before considering them for catalysis and adsorption applications.

2.3 Experimental Section

2.3.1 Co-SBE Material Synthesis

The reagents used were aluminum isopropoxide, *o*-phosphoric acid (85wt%, ethylene glycol (99%), a cobalt carbonate hydrate salt, 1,9-diaminononane (98%, DAN), dipropylamine (99%, DPA), ethanol and distilled-deionized water. All reactants were purchased from Sigma-Aldrich and used as received.

Cobalt-rich SBE samples were synthesized hydrothermally following the recipe previously reported [11, 15]. Prior to crystallization, it was necessary to prepare two solutions: (A) an AIPO rich- and (B) a cobalt-rich phase, respectively. Reactants used for solution A were aluminum isopropoxide (Sigma-Aldrich), *o*-phosphoric acid (85 wt.%, Sigma-Aldrich), and ethylene glycol (99%, Sigma-Aldrich). Solution A was aged for 1 week under stirring conditions. Meanwhile, solution B was prepared mixing a cobalt carbonate hydrate salt (Sigma-Aldrich), *o*-phosphoric acid (85 wt.%), and distilled/deionized water at room temperature for about 15 min. A third solution (C = A + B) was prepared under heavy mixing conditions until complete dissolution. The organic template, 1,9-diaminononane (98%, idem, DAN) was then added under constant stirring. A co-solvent, dipropylamine (99%, idem, DPA), was added dropwise until the pH of the final solution was brought to a value of 7.7. The resulting final gel composition has the following oxide composition: $0.5C_9H_{24}N_2O:2.5C_6H_{16}NO:CoO:0.5Al_2O_3:P_2O_5:50H_2O$.

Each saturated gel sample was then transferred to 45 mL Teflon-lined stainless-steel autoclaves (Parr Instruments Co.) and aged for 72, 120, 168 and 240 hours, respectively, and heated to 170 °C in a forced convection oven. After completion of the synthesis, the crystals were treated with ethanol under reflux at 80 °C for 24h to remove any bulk impurities. The

resulting intense blue-colored crystals were rinsed several times with copious amounts of distilled-deionized water and carefully dried at 90 °C overnight to remove the excess water.

2.3.2 Structural, Compositional and Textural Characterization

Both the as-synthesized and detemplated samples were characterized via powder X-ray diffraction (XRD) using a Rigaku ULTIMA III X-ray unit equipped with a copper anode tube (CuK_{α}, $\lambda = 1.5405$ Å), operating at 40 kV and 44 mA. The diffraction angle (2 θ) range was set to 3-40° while the step size and scan speed were 0.04° and 2°/min, respectively. Morphology and elemental composition were determined by scanning electron microscopy (SEM) using a JEOL JSM-6390 unit fitted with an energy dispersive X-ray spectrometer (EDX, 10.0 kV, SUTW-Sapphire Detector).

Porosimetry studies were performed using nitrogen at -196 °C as described elsewhere [16, 17]. A static volumetric adsorption unit (Micromeritics ASAP 2020) was used for such analyses. Before measurements, the samples were degassed at a heating rate of 5 °C/min and an evacuation rate of 50 mmHg/s for 3 and 18 h according to the type and treatment of the sample. The specific surface area was determined according to the Langmuir method in the relative pressure range of 0.01-0.20 [18] and the results are shown in Table 2.1. The results also include micropore and external surface areas obtained via the *t*-plot method [19-21]. The experimental nitrogen isotherm was transformed using the aforementioned method to estimate the contribution of the micropores to the overall surface area.

2.3.3 Template Thermal Degradation Studies

Coupled (TGA/FTIR) experiments were carried out using a TA Instruments 2950 thermogravimetric analyzer. The TGA exhaust gas/vapor was sent to a Nicolet 6700 Optical Spectrometer mainframe equipped with a Nicolet X700 TGA/IR external interface module. This module contains a high-efficiency condensing and collection optics, a DLa TGS detector, a nickel coated stainless steel gas cell, and a heated transfer line. Both the transfer line and the gas cell were kept at 250 °C to prevent condensation of any high boiling point species arising from the decomposition of the SDA onto the system detector. Although the TGA can be operated up to ca. 1000 °C, the IR interface can be operated at temperatures up to 327 °C. Dry Air or helium gases were used as carrier gas during the TGA/FTIR tests. All spectra were recorded after 32 scans in the range of 4000-600 cm⁻¹ and with a resolution of 8 cm⁻¹.

2.3.4 Detemplated Co-SBE Structural Stability Studies

The structural stability experiments were carried out in two parts. For the first part, samples of Co-SBE material were partially detemplated in vacuum using a Micromeritics VacPrep 061 sample degas at 350 °C for 6 h. Isolated retrieval of the samples was possible by employing glass sample holders fitted with isolation valves and backfilling to 1 atm with ultrahigh purity helium. After treatment, one of the samples was exposed directly to ambient laboratory conditions while a second one was thoroughly mixed with deionized water in a flask for around 72 h. Both samples were tested with TGA to estimate the percentage of water in those samples. A third vacuum detemplated sample was kept isolated from humid conditions to serve as a control. All these samples were analyzed via standard XRD.

The second part of the experiments was performed using an *in situ* high temperature X-Ray diffraction setup to evaluate the effect of water exposure on the structure stability of detemplated Co-SBE materials. A ReactorX (Rigaku Corp.) high temperature module was attached to the aforementioned ULTIMA III XRD unit for these tests. The module consists of a small volume (less than 200 cm³) chamber fitted with a continuous beryllium window (for unrestricted passage of X-rays) and an infrared heating element that permits heating up to ca. 1000 °C in the presence of a gas flow. Infrared heating allows for ultrafast cooling, which is suitable for ramp and soak testing of temperature sensitive samples. In a typical test, the sample is placed onto a black quartz plate fitted with a small side hole to accommodate the tip of a 1/16th thermocouple. Both the plate and the attached thermocouple are carefully placed inside the ReactorX mainframe and the chamber housing moved into place. The *in situ* high temperature experiments were performed using dry and moist helium atmospheres, the latter made possible by flowing the gas through two liquid bubblers connected in series and located upstream. A gas flow rate of ca. 60 mL/min was employed for all the runs. XRD patterns were recorded during three-stage tests: (I) heating of as-synthesized Co-SBE from 30 to 350 °C at 5 °C/min in dry ultrahigh purity helium, (II) fast cooling to and soaking at 30 °C for 72 h in humid helium and (III) heating from 30 to 550 °C at 5 °C/min in dry ultrahigh purity helium. Stage I is basically aimed at *in situ* detemplation while stages II and III were designed to allow for structural monitoring while adsorbing and desorbing water, respectively.

2.4. Results and Discussion

2.4.1 Synthesis and Characterization

The effect of the aging time length on the structural and textural properties was evaluated in an attempt to optimize the SBE materials preparation. Figure 2.1 shows XRD patterns and SEM micrographs for the as-synthesized Co-SBE samples, clearly evidencing the dominance of an SBE-like phase. The XRD pattern corresponding to 72 h aging time, however, presents a few unexpected peaks probably due to the presence of small crystals of an undefined phase as evidenced by the SEM micrograph. The SBE phase in this case corresponds to the crystals measuring about 500 μ m. Meanwhile, samples aged for 120 and 168 h clearly exhibit relatively sharp and intense XRD peaks and neat particle morphology, but only the latter case resulted in typical hexagonal shape Co-SBE crystals (100 to 250 μ m) [11, 15]. For the samples aged for 240 h, less intense peaks are observed in the low 2 θ region; probably due to considerable framework distortion and instability as seem in the corresponding SEM image.

All samples were treated in vacuum to remove the structure-directing agent (SDA) following the procedures developed by Belen-Cordero et al [11, 15]. Figure 2.2 shows that the surface area resulting after detemplation increased as the aging synthesis time were increased. The data appears to lead to the conclusion that longer aging times would be appropriate to maximize total surface area, but careful inspection indicates that the sample aged for 240 h exhibits what appears to be a tendency to result in larger external surface area. This should be related the SEM results previously discussed where the particles appear to have suffered stress associated probably due to a non-uniform temperature distribution during synthesis. This is

known to generate and propagate dislocations and macro-cracking during growth process [22, 23], which would lead to an increase in macroporisity. Nevertheless, the samples prepared after 168 h aging, which contain the desired morphology, exhibit a total surface area of ca. $630 \text{ m}^2/\text{g}$. This is nearly 26% larger than the results previously reported [15] evidencing how important is the aging effect on detemplation.



Figure 2.1 X-ray powder diffraction data and SEM micrographs for as-synthesized SBE samples as a function of the synthesis aging time.



Figure 2.2 Surface area distribution for SBE samples as a function of hydrothermal synthesis time. Detemplation was performed in ultra-high vacuum at 375 $^{\circ}$ C.

(Co+Al)/P atomic ratio
1.32
0.73
0.87
0.74

Table 2.1 Elemental composition data for SBE-Co samples

Atomic (Co + Al)/P ratios for the samples prepared with different aging times are gathered in Table 2.1. The data was estimated via EDS analysis as detailed in the experimental
section of this chapter. These atomic rations provide additional evidence to corroborate the presence of a SBE structure since the theoretical ratio for a pure SBE phase should be close to unity. In general, it was confirmed that aging for 168 h yields the desired phase.

2.4.2 Detemplation Process

Coupled thermogravimetric/Fourier transform infrared spectroscopy (TGA/FTIR) analyses are suitable to gather semi-quantitative information about the type and functionality of the products obtained during the SDA degradation or detemplation [24]. By employing a TGA instrument upstream it is possible to generate transient spectra surface plots that map the step-wise decomposition of the SDA while allowing for correlation to changes related to the inorganic framework. The latter may include release of extra-lattice oxygen (ELO) at high temperatures [25, 26]. The TGA/FTIR technique has been used to study the products involved during the degradation of some commercially available organoclays [27]. For instance, the non-oxidative thermal degradation of the surfactant results in the release of water, aldehydes, aliphatic, carboxylic acids, and in some cases, aromatic compounds and CO₂. In addition, the chemical structure of the surfactant plays an important role in the thermal decomposition dynamics [27].

Figure 2.3 shows a TGA profile and transient IR spectra gathered for a Co-SBE sample prepared after 168 h of aging and treated in helium. In the spectra, the bands observed in the 4000-3300 cm⁻¹ range are due to O-H stretching associated to water, also confirmed by the presence of O-H bending bands at 1700-1500 cm⁻¹ [27]. The existence of the N-H stretching mode of ammonia was noted by the presence of the bands in the 3380-3361 and 1150-950 cm⁻¹ range, respectively, while bands associated to characteristic C-H stretching vibrations for methyl and methylene groups were observed in the 2981-2800 cm⁻¹ range [28]. Carbon dioxide was

identified by the presence of two bands located at 2364 and 2348 cm⁻¹ probably a result of a high temperature reaction between the SDA carbon and the ELO from the SBE framework under helium atmosphere (Figure 2.3). Carbon monoxide was also detected during the combustion stage as evidenced by two absorption bands observed at 2125 and 2194 cm⁻¹. Also, absorption bands at 1380 cm⁻¹ could be attributed to CH₃, CH₂ deformation of C-H bending confirming the presence of these fractional species during detemplation.

C-N stretching mode bands are usually found at ca. 1090-1040 cm⁻¹ [28], but these were absent in Figure 2.3 probably indicating that bond rupturing is limited to the aliphatic chain of the SDA. In order to confirm the generation of $NH_{3(g)}$ from the decomposition of the SDA (1,9-diaminononane), an experiment was carried out to follow the thermal decomposition of NH_4Cl to produce $NH_{3(g)}$ and $HCl_{(g)}$ [29]. Identification of the corresponding IR bands was then used for identification of the ammonia in the Co-SBE IR data. The signal of ammonia was validated and confirmed in the range of 964-929 cm⁻¹.



Figure 2.3 TGA weight loss profile (*left*) and time-evolved FT-IR spectra (*right*) for the thermal decomposition products of as-synthesized Co-SBE. Data gathered under a dry helium atmosphere.

During the first 10-20 minutes of the detemplation test performed in helium (Figure 2.3), TGA pointed to a 5% weight loss corresponding to the release of bulk water. The remaining weight loss amount (total of ca. 20%), which matches well with the amount of SDA per unit cell [11, 15, 30], corresponds to the decomposition of the SDA into a series of products that evolved according to the IR data. Spectral bands corresponding to the release of water intensify after the 20 min mark due to the combustion of the SDA with the ELO. In addition, several bands appear and disappear due to formation of aliphatic compounds and its subsequent combustion to produce carbon dioxide, carbon monoxide and water. The IR data also show the formation of NH₃, which should evolve during the last stages of the degradation process, particularly after the formation of ammonium. In this case, it is quite difficult to quantify the production of the of aliphatic fractions since all of the decomposition products evolved simultaneously indicating that the kinetics occur in a time fraction orders of magnitude smaller than the one required to evolve from the TGA system. The detemplation mechanism shown in Scheme 2.1 was generated using all of the aforementioned observations and the TGA/IR data.

Scheme 2.1 Thermal decomposition mechanism of 1,9-diaminononane in Co-SBE and helium. ELO* and Z^- denote denotes extra-lattice oxygen and Co-SBE framework, respectively.

TGA data for Co-SBE treated in oxidative conditions (Figure 2.4) indicate that only a fraction of the template is eliminated. When one compares the overall weight loss observed during treatment in helium to the results obtained from treatment in air, the latter is about 22% smaller than the former indicating that a significant fraction of the SDA is left inside the pores of the material. This is probably due to encapsulation brought by framework distortion as explained by Belen-Cordero et al. [15]. They used *in situ* differential scanning calorimetry XRD (DSC-XRD) and magic angle spinning nuclear magnetic resonance (MAS-NMR) data to monitor structural long and short range structural changes during thermal treatments, which were considerable even at temperatures as low as 277 °C (550 K). Although it appears that an oxygenrich atmosphere is a rather detrimental option for detemplation (i.e., due to oxidation of cobalt centers), monitoring of the species evolving from the degradation of the SDA is essential to completely understand the role this plays in the structural transformation previously observed by Belen-Cordero et al. [31].



Figure 2.4 TGA weight loss profile (*left*) and time-evolved FT-IR spectra (*right*) for the thermal decomposition products of as-synthesized Co-SBE. Data gathered under a dry air atmosphere.

Once again, an FTIR analysis was used to help identity the functional groups of the products evolving from the SDA thermal degradation process (see Figure 2.4). As expected, the IR signals for carbon dioxide CO₂ (2364 and 2348 cm⁻¹) and carbon monoxide CO (2125 and 2194 cm⁻¹) are far more intense and start to appear earlier when compared to the results obtained for treatment in helium atmosphere (see Figure 2.3). In addition, C-H contributions (2981-2800 cm⁻¹) appear, but in lower proportions at around 450 °C (723 K). The absence of the C-N stretching mode bands (1090-1040 cm⁻¹) [28] again indicates that bond rupturing in the SDA is limited to the aliphatic chain. Other bands observed at temperatures higher than 427 °C (700 K) evidence subsequent decomposition of the SDA and correspond to a combustion reaction plausibly suffered by methylene groups (see stage III in Scheme 2.2) encapsulated in the structure with the temperature. Since this process occurs at a much higher temperature than the one observed by Belen-Cordero et al. for distortion of the SBE structure, it appears that the SDA decomposition is not responsible for such structural changes. Furthermore, the elimination of SDA fragments at temperatures higher than 427 °C (700 K) is most likely due to diffusion resistance provided by a distorted or collapsed pore structure.

$$\begin{bmatrix} \left(H_{3}N(CH_{2})_{9}NH_{3}\right)^{2^{+}} \end{bmatrix}_{16} \begin{bmatrix} AI_{32}Co_{32}P_{64}O_{256}^{2^{-}} \end{bmatrix} \xrightarrow{AIO_{2}exc} 144CO_{2(g)} + 144H_{2}O_{(g)} + 32NH_{3(g)} + \text{Residue} \\ \begin{bmatrix} ^{+}H_{3}N - CH_{2} - NH_{3}^{+} \end{bmatrix}_{16} \cdot \begin{bmatrix} Z^{-} \end{bmatrix}_{32} \\ (I) \begin{bmatrix} \left(H_{3}N(CH_{2})_{9}NH_{3}\right)^{2^{+}} \end{bmatrix}_{16} \cdot \begin{bmatrix} Z^{-} \end{bmatrix}_{32} \cdot 26H_{2}O \xrightarrow{AIO_{2}exc} \\ \begin{bmatrix} \left(H_{3}N(CH_{2})_{9}NH_{3}\right)^{2^{+}} \end{bmatrix}_{16} \cdot \begin{bmatrix} Z^{-} \end{bmatrix}_{32} \cdot 26H_{2}O \xrightarrow{AIO_{2}exc} \\ \begin{bmatrix} \left(H_{3}N(CH_{2})_{9}NH_{3}\right)^{2^{+}} \end{bmatrix}_{16} \cdot \begin{bmatrix} Z^{-} \end{bmatrix}_{32} \cdot 26H_{2}O \xrightarrow{AIO_{2}exc} \\ \begin{bmatrix} \left(H_{3}N(CH_{2})_{8}NH_{3}\right)^{2^{+}} \end{bmatrix}_{16} \cdot \begin{bmatrix} Z^{-} \end{bmatrix}_{32} \xrightarrow{AIO_{2}exc} \\ \begin{bmatrix} \left(H_{3}N(CH_{2})_{8}NH_{3}\right)^{2^{+}} \end{bmatrix}_{16} \cdot \begin{bmatrix} Z^{-} \end{bmatrix}_{32} \xrightarrow{AIO_{2}exc} \\ \begin{bmatrix} \left(H_{3}N(CH_{2})_{8}NH_{3}\right)^{2^{+}} \end{bmatrix}_{16} \cdot \begin{bmatrix} Z^{-} \end{bmatrix}_{32} \xrightarrow{AIO_{2}exc} \\ \begin{bmatrix} \left(H_{3}N(CH_{2})_{8}NH_{3}\right)^{2^{+}} \end{bmatrix}_{16} \cdot \begin{bmatrix} Z^{-} \end{bmatrix}_{32} \xrightarrow{AIO_{2}exc} \\ \begin{bmatrix} \left(H_{3}N(CH_{2})_{8}NH_{3}\right)^{2^{+}} \end{bmatrix}_{16} \cdot \begin{bmatrix} Z^{-} \end{bmatrix}_{32} \xrightarrow{AIO_{2}exc} \\ \begin{bmatrix} \left(H_{3}N(CH_{2})_{8}NH_{3}\right)^{2^{+}} \end{bmatrix}_{16} \cdot \begin{bmatrix} Z^{-} \end{bmatrix}_{32} \xrightarrow{AIO_{2}exc} \\ \begin{bmatrix} \left(H_{3}N(CH_{2})_{8}NH_{3}\right)^{2^{+}} \end{bmatrix}_{16} \cdot \begin{bmatrix} Z^{-} \end{bmatrix}_{32} \xrightarrow{AIO_{2}exc} \\ \begin{bmatrix} \left(H_{3}N(CH_{2})_{8}NH_{3}\right)^{2^{+}} \end{bmatrix}_{16} \cdot \begin{bmatrix} Z^{-} \end{bmatrix}_{32} \xrightarrow{AIO_{2}exc} \\ \begin{bmatrix} \left(H_{2} + CH_{2}\right) \end{bmatrix}_{16} \cdot \begin{bmatrix} Z^{-} \end{bmatrix}_{32} + X(CH_{2} = CH_{2})_{2.5(g)} + 32NH_{3(g)} + 56CO_{2(g)} + 56H_{2}O_{2(g)} \\ \xrightarrow{AIO_{2}exc} \xrightarrow{AIO_{2}exc} \\ \xrightarrow{AIO_{2}exc} \xrightarrow{AIO_{2}exc} \\ \xrightarrow{AIO_{2}exc} \xrightarrow{AIO_{2}exc} \xrightarrow{AIO_{2}exc} \\ \xrightarrow{AIO_{2}exc} \xrightarrow{AIO_{2}exc} \xrightarrow{AIO_{2}exc} \xrightarrow{AIO_{2}exc} \\ \xrightarrow{AIO_{2}exc} \xrightarrow{AI$$

Scheme 2.2 Thermal decomposition mechanism of 1,9-diaminononane in Co-SBE and air. ELO* and Z^- denote denotes extra-lattice oxygen and Co-SBE framework, respectively.

Although a coupled TGA/FTIR approach provides a practical tool to gather information about the degradation products of the SBE template, the data and discussion presented above are not sufficient for elucidating the precise chemical nature of all the decomposition products since these are probably produced in a time scale order of magnitude smaller than the one required by the technique. Nevertheless, the information presented here clearly indicates that the degradation of the SDA via a combustion process is definitely not an adequate alternative for detemplation of cobalt-rich SBE aluminophosphates. Furthermore, the template elimination or degradation depends greatly on the concentration and nature of the metal centers in the framework [31], so one must be cautious when extrapolating the mechanisms shown in Schemes 1 and 2 to systems other than Co-SBE.

2.4.3 Structural Stability of Detemplated Co-SBE

One important aspect about transition-metal rich microporous zeolitic materials is their resistance toward humid environments or even when exposed to bulk water amounts. This is an important criterion for process design, particularly if the adsorbent or catalysts would require a guard bed to protect the former from humidity. In order to elucidate the stability of detemplated Co-SBE materials toward humidity, we employed both *ex situ* and *in situ* XRD experiments. Figure 2.5 shows the XRD patterns for detemplated samples exposed *ex situ* to moist air and water and the pattern corresponding to the as-synthesized material.



Figure 2.5 X-ray powder diffraction data for structural stability of detemplated Co-SBE

Evidently, the peaks corresponding to the SBE phase have disappeared and the crystal structure has suffered dramatically. This should correlate with some color changes that were observed during the tests, which are indicators of the possible chemistry involved in the structural change process. For instance, once the detemplated sample was exposed to atmospheric air, its color changed from an intense blue color to a lighter one, suggesting changes related to coordination geometry, electronic environment or a different oxidation state for framework cobalt [32].

There are also some structural changes associated to the detemplation process, even for the cases involving vacuum or helium. In order to distinguish between structural changes produced by the detemplation process and those arising from water exposure we also performed stability studies *in situ*. Figure 2.6 shows a stack of XRD patters gathered during stage I (see Experimental section), which consists of a detemplation process in helium.



Figure 2.6 In situ high-temperature XRD for as-synthesized Co-SBE (Stage I)

There is a slight shift of some peaks to lower angles and significant decrease in the intensity of the peak associated to the plane [101] (ca. $2\theta = 5^{\circ}$), which could be related to thermal stress associated to a non-uniform temperature distribution though the crystal. This result together with the data shown in Figure 2.3 clearly evidences that the major structural loss observed in Figure 2.6 is predominantly due to the interaction of water with the structure.

Cooling of the sample *in situ* followed by exposure of the sample to moist helium (stage II) results in the XRD transient stack shown in Figure 2.7. Reducing the temperature to 30 °C

(303 K) results in a significant increase in the intensity the low 2θ peak, indicating that the changes observed in Figure 2.6 for that plane were indeed due to thermal stress.



Figure 2.7 In situ high-temperature XRD for detemplated Co-SBE in a humid helium flow (Stage II)

Furthermore, addition of moisture into the sample environment did not produce any remarkable structural changes even after 70 hours. This is a remarkable result that may lead to the assumption that the changes observed in the XRD data shown in Figure 2.6 are not exclusively due to water. In fact, after removing the adsorbed water using heat and dry helium the XRD data (Figure 2.8) shows no structural changes up to 330 °C (603 K). Changes were only observed only above 703 K and due to destruction of the sample upon thermal stress.



Figure 2.8 In situ high-temperature XRD for detemplated Co-SBE in a dry helium flow (Stage III)

In general, both the *ex situ* and *in situ* results indicate that the Co-SBE samples are unstable in humid oxygen-rich environments while probably stable in inert gas, even in the presence of traces of water. Adsorption of water [33] and di-oxygen [34] are known to produce changes in aluminum coordination and valence state in cobalt centers, respectively. However, only the latter species have been linked to color changes, which correlate well with the experimental observations previously discussed.

It is worth noting that the apparent stability limitation of detemplated Co-SBE in ambient air should not be considered a limit for the applicability of these materials for catalysis and perhaps adsorption based applications. To date, there are many reports about commercial catalysts that are used under controlled environments also due to stability problems to ambient air and/or humidity.

2.5 Conclusions

The results presented here suggest that the aging time employed during the synthesis of Co-SBE greatly affects the morphological, structural and textural properties of the material and that perhaps only a small time-window of opportunity exists for obtaining suitable crystals (i.e., with less macro-faulting) when employing hydrothermal means. Furthermore, by controlling the aging step and carefully performing detemplation in vacuum we were able to obtain a Co-SBE material with a micropore surface area of ca. 600 m²/g, which is remarkable for a multi-dimensional framework that contains a cobalt-to-aluminum ratio close to unity.

In terms of the detemplation mechanism, coupled TGA/FTIR studies indicate that the degradation of the aliphatic amine based SDA appears to proceed in two steps that lead to the formation of CO_2 , CO, H_2O and NH_3 . In the case of detemplation in inert atmosphere, the production of species typical of a combustion process is probably due to the presence of Extra Lattice Oxygen (ELO).

Detemplated Co-SBE appears to be stable in oxygen-free atmospheres, even in the presence of moisture. This was evidenced by both ex situ and in situ X-ray diffraction (XRD) tests. Upon contact with atmospheric air, the structure of the samples is irreversibly destroyed and this is characterized by a drastic sample color change.

2.6 References

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Chapter 3

Alternative strategies for mild detemplation of porous CoAPO-SBE materials

3.1 Introduction

This chapter describes two different strategies focused on the effective removal of the structure directing agent (SDA) from CoAPO-SBE in order to maximize its potential for industrial or technological applications while still maintaining the crystallinity of the structure. Most template removal methods rely on the use of high temperature thermal calcination processes, employing temperature in the 300-600 °C range. However, in aggressive thermal and/or chemical environments, there is often damage to important physico-chemical characteristics.

As a first attempt, we used a chemical reaction method to break down the template bonds inside the framework followed by a high temperature vacuum assisted process in order to extract the residues. The second attempt was to use a non-thermal, photochemical calcination process prior to the regular thermal treatment. This was based on recent reports that have shown that ozone-generating ultraviolet illumination provides a low-temperature alternative that could provide an efficient and simple method for the removal of organic SDA from zeolitic materials.

3.2 Previous Work

For most inorganic porous materials, the SDA is typically removed by air calcination methods, sometimes leading to the formation of amorphous materials due to the stress applied to the frameworks, which eventually collapse [1-7]. In fact, there is strong evidence in the literature that even silica rich mesoporous pseudo-crystalline materials in which there is no direct coordination of the SDA with the material walls are affected during oxidative detemplation methods [8]. Although some alternative detemplation methods have already been documented in the literature, including vacuum detemplation [9], UV/ozone treatment [5, 6, 10], solvent extraction [4, 11], solid phase extraction (SFE) [8], and supercritical fluid extraction (SCFE) [8, 12], none are capable of effectively removing protonated SDAs from transition metal rich frameworks. The only proven detemplation strategy requires development of SDAs with particular characteristics suitable for mild detemplation conditions. However, this approach results also in SDAs capable of producing limited framework types not including SBE ones.

Parikh and co-workers recently reported an interesting photochemical method for the removal of organic SDAs from several materials, including non-transition containing aluminophosphates [10]. The method involves exposing the as-synthesized sample to short-wavelength ultraviolet (UV) radiation in air, generating an ozone environment. The UV/Ozone treatment achieved removal of the organic template while retaining integrity of the microporous

materials. For transition metal containing frameworks, such technique is not feasible due to inherent multiple coordination states of the atoms (i.e., oxidation states).

Andrade and co-workers have shown that up to 78% of template used for the synthesis of Al-MCM-41 materials could be removed either by extraction with ordinary solvents or methanol-modified SCFE CO₂ [8]. Detemplation with SCFE may be achieved faster, but the fine tuning of experimental conditions is a major requirement for success. In another SCFE work, Huang et al. explored using a CH₃OH-modified CO₂ supercritical fluid for the removal of a surfactant template on MCM-48, MCM-41, SBA-1 and SBA-3, respectively. SCFE detemplation efficiencies of 76-95% and better structural ordering and stability were obtained on these materials [12].

One way of increasing detemplation rates using inert treatments (e.g., vacuum) or any of the aforementioned techniques is the incorporation of cleavage reactions to break amine C-N and/or C-C bonds. For example, zeolites and molecular sieves synthesized using a ketal-containing SDA that has the potential to be degraded into fragments within the pore space and can be readily detemplated at mild conditions.[13, 14]. Removal of the cleavage fragments of such SDA from ZSM-5 resulted in an appropriate pore volume, kept the framework aluminum in place (measured by 27Al NMR), and enhanced the material catalytic properties.[13]

3.3 Experimental Section

3.3.1. Material Synthesis

CoAPO-SBE was prepared by hydrothermal crystallization methodology. Details on the method and procedure were described previously in the experimental section of Chapter 2.

3.3.2. Cleavage Reaction

With the intention of developing a chemical strategy to remove the SDA, we began by using solutions of sodium methoxide (95%, powder Sigma-Aldrich) in methanol (\geq 99.8% Sigma-Aldrich) [15]. The first approach was to test the 1,9-diaminononane with the base using a molar ratio of 1:10 and a temperature of 333 K for two days.

3.3.3. Removal of Structure Directing Agent (SDA) from As-synthesized CoAPO-SBE Samples

0.15 g of as-synthesized CoAPO-SBE were dispersed onto an aluminum foil holder and exposed to UV/ozone treatment for 2-8 hrs. Our room-temperature photochemical methodology involved three overlapping photoinduced chemical reactions. First, UV ozone generating short-wavelength ultraviolet (UV) light ($\lambda = 184-257$ nm), produced by a low-or medium-pressure Hg discharge lamp (10-20 mWcm⁻², UVP, Inc., Upland, CA) was employed to facilitate the dissociation of oxygen (from oxygen rich ambient) to produce ozone and atomic oxygen. Simultaneously, the 254nm line emitted by a second lamp in a quartz envelope excites and/or dissociates the organic template in the zeolitic material and, finally, the activated organic species are readily attacked by atomic oxygen and ozone synergistically to form simpler volatile molecules, such as CO₂, H₂O, and N₂. The process is completed only after the sample is treated with UV/Ozone and then placed in a degassing Micromeritics VacPrep unit at 350 °C for 6 hrs and a pressure of 50 mTorr. The oxygen flows using in the experiments was 50 mL/min (regulated from the flowmeter). Figure 3.1 summarizes the procedure described above.



Figure 3.1 UV/Ozone coupled to thermal removal process

3.3.4. Material Characterization

Both the as-synthesized and treated samples were characterized using different including, X-ray powder diffraction (XRD), scanning electron microscopy (SEM), Fourier transformed infrared spectroscopy (FTIR), Raman spectroscopy, and porosimetry, all of which were described in Chapter 2.

3.4 Results and Discussion

3.4.1. Cleavage Reaction

Figures 3.2 and 3.3 show IR and Raman spectra for the SDA after cleavage treatment. In both cases, we found a decrease in the intensity of the band of C-N stretch of PP' structure (CH₂-

NH₂) that occurs in the 1090-1040 cm⁻¹ region with strong to medium IR and Raman intensities [16], indicating this that the amine C-N bonds have been successfully broken.



Figure 3.2 FT-IR spectra of 1,9-diaminononane treated with MeONa/MeOH

Based on the control results, we decided to carry out the cleavage reaction with as-synthesized CoAPO-SBE materials. SEM micrographs (Figure 3.4) showed the effect of the cleavage alkaline medium (pH \sim 13). It is clear that the treatment modified the particle morphology in a great many ways. However, a powder XRD pattern obtained after treatment (see Figure 3.5) revealed that most of the original SBE framework characteristics were still present.



Figure 3.3 Raman spectra of 1,9-diaminononane treated with MeONa/MeOH



Figure 3.4 Scanning electron micrographs of Co-SBE at (A) 100X and (B) 250X magnification



Figure 3.5 X-ray powder diffraction patterns for SBE-Co treated with MeONa/MeOH. *Single Crystal Simulated Data Source*: Stucky and co-workers (*Science* 1997, *278*(5346), 2080-2085)

Porosimetry data (Figure 3.6) meanwhile showed an increase in sample surface area (ca. 94 m²/g), after cleavage treatment. This indicates that perhaps the cleavage reaction managed to remove some SDA species from the outer crystal layer.

According to the preliminary experiments to remove the SDA, using an elimination reaction we could assume that the complete removal of template may be successfully attained by optimizing different parameters involved in the reaction. These include concentration, pH and time, to prevent any damage to the crystalline structure.



Figure 3.6 Surface area distribution for different Co-SBE samples.

3.4.2. UV/Ozone Treatment for CoAPO-SBE Template Removal

The room temperature photochemical UV-Ozone treatment exposed the CoAPO-SBE samples to a freshly-cleaned UV lamp with the samples maintained 1-2 cm below the lamp surface. All samples were treated in vacuum to remove the SDA following the procedures developed previously and described in Chapter 2. Figure 3.7 shows that the surface area distribution for CoAPO-SBE treated with UV/Ozone coupled to a thermal detemplation process is almost uniform. However, a slight increase was observed at 2 h, suggesting that the exposure at that time was adequate to remove the SDA from CoAPO-SBE samples. In addition, these results did not include other parameters that could improve the process.



Figure 3.7 Surface area distribution for CoAPO-SBE sample as a function of UV/Ozone exposition time. Detemplation was performed in ultra high vacuum at 350 °C.

An important observation of the physical appearance of the sample once the process was completed under UV/ozone coupled with thermal treatment is the color of the sample, which looks bluer and its an indicative of the presence of cobalt in the framework. These results would point out a less detrimental effect suffered by the structure by applying this approach for the removal of the template.

Figure 3.8 shows the XRD patterns of the samples after such treatment. There are evident changes in the structure after UV/ozone coupled with thermal treatment, but the SBE framework retained some of its crystallinity characteristics after whole process, suggesting that the photo-oxidation treatment may be a good alternative for template removal of these kinds of aluminophosphates. Is important to mention that the samples were unavoidably exposed to

laboratory atmospheric conditions during the gathering of the XRD data and this may as well affect the integrity of the SBE framework. This was discussed in the previous chapter.



Figure 3.8 XRD powder diffraction data for CoAPO-SBE samples as a function of UV/Ozone exposition time coupled with thermal treatment at 350 $^{\circ}$ C.

3.5 Conclusions

The removal of the SDA from CoAPO-SBE using a cleavage reaction indicated that the SBE framework can be severely affected according to the SEM images shown after treatment; this may be related to the oxidation process of cobalt centers due to the pH involved in the process.

It was shown that room temperature UV/Ozone treatment could provide an efficient option for the SDA removal while simultaneously stabilizing the inorganic SBE framework. However, further studies would be needed to support this hypothesis.

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Chapter 4

Modification of a cobalt-aluminophosphate (Co/Al~1) with a multidimensional pore system via coupled partial detemplation and solid state ion exchange with alkali metals for the adsorption of light gases

SBE type metal substituted aluminophosphates (MeAPOs) are materials with multidimensional pore frameworks that are highly unstable to oxidative and high temperature conditions due to the large content of transition metal centers. In this study we have shown, however, that it is possible to effectively functionalize these materials using coupled vacuum assisted partial detemplation and solid-state ion exchange (PD/SSIE) at mild temperatures. A cobalt-rich SBE type aluminophosphate (CoAPO (SBE); Co/AL ~ 1) was detemplated and SSIE with either Na⁺ or Li⁺ in an attempt to modify its surface properties while preserving the framework and textural characteristics. The resulting porous materials were also tested for the equilibrium adsorption of CO₂ to elucidate the level of adsorbate-adsorbent interactions and,

therefore, the potential of these materials for gas separation processes via adsorption. At 25 $^{\circ}$ C, the best CO₂ loading capacities were observed in the sodium-SBE variants at both low and high partial pressure ranges. Furthermore, this adsorbent material exhibited good selectivity toward CO₂ over CH₄ or N₂, particularly at low partial pressure and likely due to the interaction of accessible sodium extraframework cations with the strong quadrupole moment of the CO₂ molecules. Although the adsorbent materials discussed here have yet to display capacities that match those of some commercial porous materials, the findings should serve as a basis to make possible the development of MeAPOs with multidimensional pore systems and superior surface characteristics.

4.1 Introduction

The present chapter presents the employed a PD/SSIE strategy at mild temperatures to successfully produce a porous M^+ -CoAPO (SBE) (M = Li or Na) adsorbent. The process was carried out in vacuum to avoid exposure of the framework to ambient conditions that are detrimental to its stability. Afterwards, the materials were tested for the adsorption of CO₂ to elucidate its interaction with lithium or sodium. The material showcasing the highest adsorption capacity was also tested for the adsorption of CH₄ and N₂ to estimate the level of selectivity.

4.2 Previous Work

Metal-substituted aluminophosphates (MeAPOs) are of particular interest for the design of materials for catalysis, ion exchange, photoluminescence and adsorption applications [1-7]. Two of the main challenges encountered in the design of MeAPOs are obtaining high framework metal loadings (i.e., Me/Al ~ 1) and producing stable AIPO open frameworks with multidimensional pore systems. During the late 1990s, Stucky and co-workers showed that linear diamines could be employed as structure-directing agents (SDAs) to produce a number of transition metal containing aluminophosphates with multi-dimensional pores (UCSB-*n* series) [8]. However, the complete removal of the SDAs to expose microporosity remained an elusive task for nearly a decade, likely due to the low stability of the frameworks under thermal oxidative conditions. Recently, Hernandez-Maldonado and co-workers developed a vacuum assisted thermal method to remove 1,9-diaminononane (DAN) molecules from a CoAPO (SBE) (also known as UCSB-8; see Figure 4.1 for unit cell) with minimal damage to the framework and exhibiting surface areas of ca. 700 m²/g [9-11].

The latter matched very well with those exhibited by commercial zeolites such as synthetic Faujasites. However, Hernandez-Maldonado and co-workers also discovered that the detemplated material is unstable to atmospheric air probably due to damage or faults induced by humidity and/or oxygen [11]. This evidently imposes another challenge if post-synthesis functionalization of the material is desired.

Modification of the surface of zeolitic materials for catalysis and adsorption applications is typically accomplished via liquid state ion exchange (LSIE) [12], a straightforward mean to introduce extraframework species that would impart unique interactions with guest molecules. For materials that are unstable in aqueous medium, however, methods such as solid-state ion exchange (SSIE) [7, 13-26] are preferred. These could be energy intensive, but they also require less amounts of the ingoing cation source resulting in less waste accumulation after completion. In addition, these methods permit metal loadings that surpass values typically obtained with

LSIE most likely due to the absence of aqueous equilibrium limitations. For SSIE to be successful, it is also essential to employ temperatures that are above the Tammann point [27]. This is defined as the temperature where the ingoing cation salt becomes appreciably mobile in the bulk of the solid, and it is approximately (1/2) T_m , where T_m is the melting point in absolute temperature units (i.e., K). For CoAPO (SBE) materials, the SSIE should be implemented not only at mild temperatures (i.e., low T_m), but also in series or parallel with the detemplation process and under inert atmospheres to avoid framework damage. Hernandez-Maldonado and co-workers have developed a coupled partial detemplation/solid state ion exchange (PD/SSIE) methods to produce silicoaluminophosphates (SAPOs) with multiple alkaline earth cations per unit cell in an effort to produce materials for the deep removal of CO₂ from air in portable applications [26]. The partial detemplation process produced ammonium species that could be easily exchanged by strontium (II) since the former species are located in prominent sites across the unit cell as opposed to protons, which are usually found in forbidden sites (i.e., prisms)[28, 29].

Figure 4.1 SBE framework (left) unit cell/supercage and (right) view along *c*.

4.3 Experimental Section

4.3.1 CoAPO-SBE Synthesis

CoAPO (SBE) crystals were obtained using hydrothermal synthesis procedures reported elsewhere [8-11]. Reagents used were: aluminum isopropoxide, *o*-phosphoric acid (85wt%), ethylene glycol (99%), cobalt carbonate hydrate, 1,9-diaminononane (98%, DAN), dipropylamine (99%, DPA), ethanol and distilled-deionized water. All the reactants, except water, were obtained from Sigma-Aldrich and used as received. The resulting cobalt-rich SBE intense blue-colored crystals were recovered via filtration, washed several times with copious amounts of distilled-deionized water and dried at 90 °C in a forced convection oven overnight to remove the excess water.

4.3.2 Partial Detemplation and Solid-State Ion Exchange

 M^+ -CoAPO (SBE) (M = Li or Na) samples were prepared via coupled PD/SSIE. The sodium and lithium sources employed were alkali chlorides purchased from Sigma-Aldrich and used as received. The ingoing cation salt loadings employed during the SSIE corresponded to the amount necessary to achieve about 50% of the total CoAPO cation exchange capacity (CEC). For the preparation of Na⁺-CoAPO (SBE), the NaCl was first crushed in a mortar for 2-3 min at ambient conditions until a fine powder was obtained and then carefully mixed with the assynthesized CoAPO in plastic vials. Mixing was accomplished via agitation with a mechanical shaker at 200 rpm for 20-30 minutes. The resulting powder was then transferred to round bottom glass sample holders fitted with isolation valves. These sample holders were then placed in a Micromeritics VacPrep 061 vacuum-based degassing unit equipped with a temperature control

interface. Vacuum was set to 500 mTorr in an attempt to minimize sublimation of the salt during the thermal treatment. A ramp and soak method was employed during the thermal treatment as follows: (1) heating at 10°C/min from room temperature to 200 °C followed by soaking at 200 °C for 24 hrs; (2) heating at 10 °C/min to 325, 350, 375 or 400 °C, and soaking at this temperature for 168 hrs (7 days). The final SSIE temperature was chosen close to the Tammann value to permit the spontaneous dispersion of NaCl ($T_m = 264$ °C) onto the solid surface but within the thermal stability limits of the SBE framework [9-11]. In addition the SSIE temperature was chosen close to the minimum temperature necessary for the effective removal of the SDA (ca. 350 °C) [11]. After the PD/SSIE process was carried out to completion, the samples were backfilled with ultrahigh purity helium (Praxair) to 1 atm and transferred to a volumetric adsorption apparatus that will be described in the following sections.

For the ion exchange with LiCl ($T_m = 168^{\circ}$ C), the sample preparation and mixing procedure was performed inside a glove box due to the hygroscopic nature of the ingoing cation salt. The PD/SSIE part, however, was performed at conditions identical to those employed for the sodium case. Detemplated samples (i.e., H⁺-CoAPO (SBE)) were also prepared and used to obtain a base reference during some of the characterization routines and adsorption tests. These samples were prepared in the VacPrep unit at 350 °C for 6 hrs and a pressure of 50 mTorr.

4.3.3 Materials Characterization

Powder X-ray diffraction (XRD) tests were performed on the as-synthesized CoAPO (SBE) sample using a Rigaku ULTIMA III system outfitted with a copper anode (CuK_{α}, λ = 1.5405 Å) and operating at 40 kV and 44 mA. A scanning speed of 3.7°/min and a step size of 0.04° over the (20) range of 3-40° was employed. Elemental composition analyses for the

PD/SSIE samples were performed using inductively coupled plasma mass spectrometry (ICP-MS). These tests were performed at Galbraith Laboratories, Inc.

4.3.4 Porosimetry and Adsorption Measurements

Total specific surface area values for each M^+ -CoAPO (SBE) variant were estimated using nitrogen adsorption equilibrium data gathered at -196 °C in a Micromeritics ASAP 2020 instrument. This unit is equipped with turbo molecular drag pumps that permit evaluation of adsorption data at ultra-low pressure. Furthermore, the instrument is fully compatible with the sample holders employed for the PD/SSIE method described above, which avoids unnecessary exposure of the samples to ambient conditions. The specific surface areas were calculated according to the Langmuir method in the relative pressure range below 0.20 [30]. Meanwhile, the micropore and external surface area values were estimated by means of *t*-plot analysis for microporous adsorbents [31-33].

Pure component equilibrium adsorption isotherms for CO_2 (ultrahigh purity grade, Praxair), CH_4 (high purity grade, Praxair) or N_2 (high purity grade, Praxair) at 25 °C on M⁺-CoAPO (SBE) were gathered also using a volumetric adsorption method. A Micromeritics ASAP 2020 and an ASAP 2050 units were employed to gather the data at low and high partial pressures, respectively. The adsorbents were transferred from the VacPrep unit to the ASAP 2020 or 2050 analyses ports without any exposure to ambient.

4.3.5 DRIFTS Study of the Adsorption Interactions of CO₂ with CoAPO-SBE Materials

Diffuse reflectance infrared Fourier transform spectra (DRIFTS) were acquired using a Thermo Scientific Nicolet iS10 FTIR spectrometer. The data of the CoAPO-SBE as-synthesized, CoAPO-SBE detemplated and Na⁺-CoAPO-SBE dehydrated samples were collected at a resolution of 4 cm⁻¹ employed 100 scans per sample. A background, with pure KBr, provided by Nicolet, applying the same conditions was always gathered previous to sample collection. The CoAPO-SBE, H⁺-CoAPO-SBE and Na⁺-CoAPO-SBE samples spectra were obtained at room temperature under N₂ (99.99%, Praxair) flowing at a rate of 50 cm³/min. Before the analysis the CoAPO-SBE and Na⁺-CoAPO-SBE dehydrated samples were previously treated at 100 °C, for 2 h under a N₂ flow applying the previously reported conditions. The H⁺-CoAPO-SBE material was prepared at 350 °C for 5 hours under N₂ (Praxair, 99.99%) flow of 50 mL/min "in situ" in the IR high temperature cell to partial removal of the template. For the acquisition of the DRIFTS spectra for CoAPO-SBE samples with adsorbed CO₂, the background was carefully measured using the dehydrated sample at room temperature. Afterwards, CO₂ (99.99%, Praxair) was allowed into the sample chamber of the IR high temperature cell at flow at a rate of 50 cm^3/min for five minutes followed by purging under N₂ (99.99%, Praxair) at the same flow rate for 5 minutes. Spectra of the CO₂ molecule adsorbed on the CoAPO-SBE framework were obtained at room temperature under N₂ flow.

4.3.6 Isosteric Heats of Adsorption

 CO_2 single component equilibrium adsorption tests were performed also at 0 and 50 °C to generate isotherm data necessary to estimate isosteric heats in M⁺-CoAPO (SBE). The heats of

adsorption were calculated using the Clausius-Clapeyron equation evaluated at constant surface loading:

$$\frac{d\ln P}{d(1/T)}\Big|_{a=cont.} = -\frac{\Delta H_{ads}}{R}$$
(1)

In this equation R is the gas constant, P is the equilibrium pressure at a particular coverage q and T is the absolute temperature.

4.4 Results and Discussion

Prior to the discussion of results it is important to justify the use of a vacuum assisted PD/SSIE and alkali metal chloride salts for the modification of CoAPO (SBE) materials. The use of an oxygen and moisture free environment is critical to avoid destruction of the crystalline SBE framework. However, the introduction of extraframework species must be performed via a reaction process that eliminates secondary products as gaseous species. PD/SSIE in assynthesized CoAPO materials involves a reaction between ammonium and proton sites with an alkali metal chloride to produce $HCl_{(g)}$, which is easily eliminated using the vacuum process. Finally, the addition of an extraframework alkali metal should enhance the uptake of gases such as CO_2 due to an increase in the basicity level of aluminophosphate as described in the literature [34-38].
4.4.1 Partial Detemplation and Solid-State Ion Exchange

Figure 4.2 shows a XRD pattern obtained for the as-synthesized CoAPO material, which matched well with the data previously published for SBE powders [9-11].



Figure 4.2 X-ray diffraction pattern of as-synthesized CoAPO (SBE).

As described in the experimental section, this material was later modified via coupled PD/SSIE to introduce sodium or lithium cations and the resulting unit cell composition data are gathered in Table 4.1. From the results it is evident that the PD/SSIE approach allowed the extra-framework incorporation of the alkali metal cations, but the observed loadings were well below the expected values (i.e., 50% of CEC). This could be explained in terms of the partial

detemplation stage and/or the sublimation of the ingoing cation source prior to ion exchange. According to Cabanzo-Olarte et al., the partial decomposition of 1,9-diaminonane (DAN) results in the formation of both ammonium cations and protons [11]. Although the distribution and location of these species along the SBE framework are yet to be determined, it is fair to assume that the ammonium cations will occupy sites readily exposed to NaCl or LiCl for ion exchange. On the other hand, protons could be located in places that would be sterically restricted to the ingoing cation source. For example, there is a set of 8-ring windows formed by the stacking of the SBE cavity ATN secondary building units (SBUs) along a or b (see Figure 4.1) that are distorted and could inhibit the transport of NaCl or LiCl. This could very well explain the amount of protons remaining in the ion exchanged materials (see Table 4.1).

According to nitrogen porosimetry analyses performed on samples detemplated or SSIE at 350°C, the surface area distribution varied considerably (see Figure 4.3). This might be attributed to the interaction of the extraframework species with the adsorbate (i.e., N₂) or partial pore blockage resulting from unexchanged ingoing cation material. Dinitrogen has a significant permanent quadrupole moment that could interact with the relatively large electric field provided by sodium cations [39, 40], resulting this in larger gas uptakes at low pressures and, therefore, an apparent larger surface area since packing will be probably more efficient.

Sample	Description	Unit Cell Composition	% Ion Exchange
DAN ²⁺ -CoAPO(SBE)	As-synthesized material	$ H_{3}N(CH_{2})_{9}NH_{3} _{16}^{2+}[Al_{32}Co_{32}P_{64}O_{256}]$	-
H ⁺ -CoAPO(SBE)	Material detemplated in vacuum at 350 °C	$ H^{+} _{32}[Al_{32}Co_{32}P_{64}O_{256}]$	-
Na ⁺ -CoAPO(SBE)	Material prepared via SSIE of H ⁺ -CoAPO(SBE) with NaCl	$ \mathbf{H}^{+} _{22} \mathbf{Na}^{+} _{10}[\mathbf{Al}_{32}\mathbf{Co}_{32}\mathbf{P}_{64}\mathbf{O}_{256}]$	31
Li ⁺ -CoAPO(SBE)	Material prepared via SSIE of H ⁺ -CoAPO(SBE) with LiCl	$ H^{+} _{21} Li^{+} _{11}[Al_{32}Co_{32}P_{64}O_{256}]$	33

 Table 4.1 Unit cell composition and percentage ion exchange for several CoAPO(SBE) materials



Figure 4.3 Surface area distribution for M^+ -CoAPO (SBE) samples. Adsorbents solid-state ion exchanged or detemplated at 350 °C.

A similar behavior has been observed in Beta zeolites $(H^+ \text{ vs. Na}^+)$ [41]. For the case of the Li⁺-CoAPO sample, the low surface area might be attributed to unexchanged ingoing cation salt. Yet another possibility could be pore blockage due to local framework faulting arising from thermal stress, which has been reported before by our group [10].

4.4.2 Carbon Dioxide Equilibrium Adsorption and Isosteric Heats

Carbon dioxide adsorption isotherms gathered at 25 °C on Na⁺-CoAPO (SBE) adsorbents SSIE at different temperatures are shown in Figure 4.4. SSIE at 350 °C appeared to yield M⁺-CoAPO (SBE) materials with suitable textural properties as evidenced by the considerable CO_2 uptake through the whole pressure range. Also, the sodium-SBE variant adsorbed more CO_2 when compared to the H⁺-CoAPO samples probably due to better interaction between the permanent quadrupole moment of the adsorbate and the electric field provided by the sodium cation sites. When the SSIE was performed at 400 °C, the process resulted in collapsing of the SBE pore framework as evidenced by the marked decreases in CO₂ loading at ca. 1 atm partial pressure.



Figure 4.4 Adsorption isotherms for CO_2 on H⁺- and Na⁺-CoAPO (SBE) samples at 25 °C. Na⁺-CoAPO (SBE) adsorbents were solid-state ion exchanged at different temperatures.

This matches well with the *in situ* high temperature XRD and MAS NMR studies performed by Belen-Cordero et al. on CoAPO (SBE) materials, which indicated that the framework undergoes severe distortion due to cobalt coordination changes eventually collapsing at temperatures above 375 °C [10]. For the sample SSIE at 325 °C, the decrease in CO₂ loading observed in the low partial pressure region (log-log plot in Figure 4.4) is plausible evidence of significant organic residue remaining inside the pores due to incomplete decomposition of the SDA (i.e., DAN) at the chosen SSIE temperature [11].

Figure 4.5 compares high pressure CO_2 equilibrium adsorption data gathered for Na⁺and Li⁺-CoAPO (SBE) adsorbents, both SSIE at 350°C, and H⁺-CoAPO (SBE). The highpressure loading trends matched well with the materials surface area (Figure 4.3), which suggests that the observed textural properties were probably a result of the SSIE process and not due to particular interactions interaction between the porosimetry probe molecule (N_2 @ -196 °C) and the different cations. A close inspection of the data gathered up to ca. 1 atm (Figure 4.5) also indicated that the CO₂ interaction with sodium cations is larger when compared to that of the Li⁺-CoAPO material. In addition, the isotherms start to show non-linearity at CO₂ loadings of ca. 1.0 and 1.3 mmol/g for Na⁺- and Li⁺-CoAPO (SBE), respectively. Using the unit cell compositional data shown in Table 4.1, these loadings correspond to about 1 CO₂ molecule adsorbed per alkali metal cation in the unit cell. In other words, the loadings observed beyond these points were a result of pore filling with the adsorbate. For the case of H⁺-CoAPO (SBE), the isotherm begins to deviate at a CO₂ loading of ca. 1 mmol/g, which corresponds to about 9 CO₂ molecules per unit cell and suggests that some of the proton sites were not available for interaction with the adsorbate.



Figure 4.5 High (left) and low (right) pressure range adsorption isotherms for CO₂ on M⁺-CoAPO (SBE) samples at 25 °C. Adsorbents solid-state ion exchanged at 350 °C. Dashed lines represent Modified Dubinin-Astakhov model fits.

The equilibrium data shown in Figure 4.5 was also fitted with different isotherm models in an attempt to elucidate the apparent governing adsorption principles in the SBE materials. However, it is important to mention that the fitting was performed in two steps to take into consideration that the adsorption volumetric units (i.e., ASAP 2020 and 2050) employed for this study provided better measurement resolution at either the low- and high-pressure range. When fitting the isotherm models, the saturation loading amounts were approximated by extrapolation of the high-pressure region data while the isotherm models parameters were refined using the low-pressure data. An attempt was made to fit a traditional Langmuir isotherm [42], but there was significant deviation at the low-pressure range (data not shown here). Although this isotherm model assumes, among other things, a flat surface geometry and a homogenous energy distribution, it has been successfully employed in the past to predict adsorption loadings in many microporous systems. In order to take into account for surface heterogeneity, we also considered a fit with a Langmuir-Freundlich (LF) isotherm model [42] (data not shown here). Again, the model considerably deviated at low partial pressures, particularly for the Li⁺- and H⁺-CoAPO (SBE) cases. A Dubinin-Astakhov (DA) isotherm model [42], which incorporates both heterogeneity and pore filling effects (i.e., interaction of the adsorbate volume with the surface), was also tested and failed to describe the low-pressure data (data not shown here). Since both the LF and DA models do not follow the Henry's law limit, we employed a Modified Dubinin-Astakhov (MDA) model [42, 43] in attempt to take this thermodynamic restriction into consideration. The MDA model is given by the following equation:

$$q = q_0 \left[\beta_1 \exp\left[-\left(C \ln\left(P_o / P\right)\right)^n \right] + \beta_2 K P \right]$$

$$\beta_1 = 1 - \exp\left(-\alpha \frac{P}{P_o} \right)$$

$$\beta_2 = \exp\left(-\alpha \frac{P}{P_o} \right)$$

$$C = \frac{RT}{\beta E}$$

$$K = \frac{q_1}{P_o}$$
(2)

where *q* is the equilibrium adsorption loading amount, q_0 is the adsorption loading amount at saturation (complete pore filling), *R* is the universal gas constant, β is the affinity coefficient of the adsorbate, *E* is the energy of adsorption, P/P_o is the relative pressure, *n* is the heterogeneity coefficient, α is a fitting parameter and *K* is Henry's law constant.

Table 4.2 summarizes the results obtained for the parameter of the MDR fitting and the model isotherms are shown in Figure 4.5. Although the standard deviation values based on the residuals observed for the model fitting were generally low, Figure 4.5 shows that there was considerable deviation at ultra-low partial pressures for the case of the Li⁺-CoAPO (SBE) sample. However, it is quite clear that the CO₂ adsorption process in the CoAPO (SBE) materials is governed by an energy distribution corresponding to a heterogeneous system and that the uptake followed a pore filling effect typical of a microporous material. In fact, the former statement correlated well with the analysis of isosteric heats of adsorption profiles (see Figure 4.6) and this will be discussed next.

	Modified Dubinin-Astakhov (MDA) Parameters						
Sorbent	q_o (mmol g ⁻¹)	С (-)	q_1 (mmol g ⁻¹)	α (-)	n (-)	Std. Deviation*	
H ⁺ -CoAPO(SBE)	5.566	0.313	161.558	184.117	2.233	± 0.005	
Na ⁺ -CoAPO(SBE)	4.521	0.287	125.287	158.273	2.451	± 0.001	
Li ⁺ -CoAPO(SBE)	4.042	0.264	281.475	973.480	2.050	± 0.004	

Table 4.2 Isotherm models parameters for CO₂ adsorption onto CoAPO(SBE) materials.

* Standard deviation calculated based on residuals between the observed and calculated equilibrium loading amounts for the complete pressure range.

Isosteric heats of adsorption profiles (Figure 4.6) indicated that CO₂ interactions with the surface of any of the adsorbent variants were at the physisorption level. Furthermore, the adsorption energy increased as follows: Li^+ -CoAPO < Na^+ -CoAPO < H^+ -CoAPO. Although the Na⁺-CoAPO samples showcased the largest CO₂ loadings at any partial pressure, the stronger adsorbate-adsorbent interaction energy was observed for the adsorbent containing only protons as extraframework species. This could be due to shielding of Na⁺ and Li⁺ effect brought by framework oxygen atoms, resulting in additional but weak CO₂ interactions with basic oxygen sites in the framework rather than with the extra-framework cations [35, 37, 44].

4.4.3 Carbon Dioxide Adsorption Study via FTIR

Figure 4.7 shows IR spectra (2700-2000cm⁻¹) range obtained after dosing the H⁺-CoAPO-SBE and Na⁺-CoAPO-SBE samples with carbon dioxide at 25°C. By increasing the CO₂ equilibrium pressure, the main broad IR band is seen at 2356 cm⁻¹ and 2361cm⁻¹ for Na⁺- CoAPO-SBE and H⁺-CoAPO-SBE, respectively. All these bands are completely reversible by outgassing at room temperature.



Figure 4.6 Isosteric heats of adsorption of CO_2 on M⁺-CoAPO (SBE) samples at 25 °C. Adsorbents solid-state ion exchanged at 350 °C.



Figure 4.7 FTIR spectra of carbon dioxide adsorbed at room temperature onto H^+ -CoAPO (SBE) and Na⁺-CoAPO(SBE) materials. The dotted line marks the frequency of CO₂ during the adsorption process.

In the free CO₂ molecule, the corresponding fundamental vibration modes are four, that is, the symmetric stretching, v_1 (1338 cm⁻¹), the doubly degenerate bending vibration v_{2a} and v_{2b} (667 cm⁻¹) and the asymmetric stretching vibration v_3 (2349 cm⁻¹) [45-47]. The band 2361 cm⁻¹ is upward shifted with respect to the 2349 cm⁻¹ value for free CO₂ [45]. A similar behavior has already been observed for Na⁺-CoAPO-SBE modified material with CO₂, forming Na+....O-C-O adducts with a linear, configuration [47] and it has been shown that this shift roughly depends on the Lewis acidity of the adsorbing center [48]. The slow decay in the concentration of physisorbed CO₂ during desorption at room temperature implies a strengthening of the interaction with the Na⁺-CoAPO-SBE samples, rather than with H⁺-CoAPO-SBE, suggesting different adsorption sites and also the presence of an electrostatic interaction with Na⁺ that still remains after CO₂ removal by outgassing. It could also be related to the formation of Na⁺ (CO₂)_n previously documented for basic zeolites [47, 49-51], but no additional bands corresponding to carbonates or bicarbonate were observed during our analysis. The shoulder at 2277 cm⁻¹ could be associated with CO₂ adsorbed onto Na⁺ cations less exposed and with a Lewis acid character lower than those Na⁺ cations present at higher frequency. This could be also attributed to the inhomogeneity of the surface as shown by the isosteric heat of adsorption profiles in Figure 4.6. At these conditions, the activated combination modes $v_{3+}v_1$ and $v_{3+}2 v_2$ of the adsorbed CO₂ were also present in our spectra at 3733 cm⁻¹ and 3625 cm⁻¹, respectively (data not shown here).

4.4.4 Na⁺-CoAPO (SBE) Adsorption Selectivity

Results obtained for the single component equilibrium adsorption of CO₂, CH₄ and N₂ at 25 °C onto Na⁺-CoAPO (SBE) are shown in Figure 4.8. The adsorbent was prepared via PD/SSIE at 350 °C since this condition resulted in the best CO₂ adsorption capacities at low pressures (see Figure 4.4) and superior overall CO₂ uptake capacity (see Figure 4.5). At 1 atm, the Na⁺-CoAPO (SBE) material displayed single point molar selectivity values of ca. 11 and 6 for CO₂ over CH₄ and N₂, respectively. These values increased significantly at lower partial pressures as evident from the isotherm data shown in Figure 4.8 and suggested that these materials are plausibly suitable for ultra-deep purification of natural gas (in the absence of water). In terms of loading amounts, it is important to mention that our adsorbent displayed capacities comparable to those of other aluminophosphates reported in the literature [52].

Since the adsorbate-adsorbent interactions are at the physisorption level (i.e., Figure 4.6), the selectivity displayed by Na^+ -CoAPO (SBE) toward CO₂ should be due to the interaction between the electric field generated by the sodium cations and the permanent quadrupole

moment of the adsorbate [46, 47]. Although N_2 also possess a permanent quadrupole moment, its value is about three times smaller than that of CO_2 [40]. Since CH_4 does not have a permanent quadruple moment and the electronic polarizabilities of all three adsorbates are similar, the electrostatic interaction should benefit the uptake of CO_2 .



Figure 4.8 Pure component adsorption isotherms for CO_2 , CH_4 or N_2 on Na^+ -CoAPO (SBE) at 25 °C. Adsorbent solid-state ion exchanged at 350 °C.

It should be mentioned that all of the adsorption processes discussed above were fully reversible upon treatment in vacuum (data not shown here), likely due to the physisorption level interactions. This is essential for the development of adsorbent materials that are fully regenerable and, therefore, minimize the need for energy intensive processes.

4.5 Conclusions

A PD/SSIE strategy was successfully implemented to produce M^+ -CoAPO (SBE) (M = Li or Na) adsorbents with good textural properties. This method provided, for the first time, a way to increase the basicity of a cobalt-rich aluminophosphate with multidimensional porous structure that is highly unstable to oxidative conditions and/or high temperatures. Furthermore, the resulting adsorbents displayed CO₂ uptake capacities that compare well with those of other aluminophosphates and excellent selectivity over CH₄ or N₂. These results should provide a basis for the development of future MeAPOs catalysts and adsorbents with multidimensional pore systems and containing high framework transition metal concentrations (Me/Al ~ 1).

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Chapter 5

Cobalt rich SBE type aluminophosphate (CoAPO-SBE) long range structural characterization

5.1 Introduction

This chapter deals with the results obtained during an internship performed as a part of degree requirement of graduate program of the UPRM Chemistry Department. This internship was conducted at the Institute for Physical Chemical Applied Research, School of Science, at the University of Turabo and the objectives were the following: (1) to perform a preliminary refinement of the structure of as-synthesized CoAPO-SBE via advanced X-ray diffraction (XRD) techniques; (2) to perform *in situ* high temperature/ high resolution XRD tests for CoAPO-SBE nanoporous samples; and (3) to study CoAPO-SBE structural changes during CO₂ adsorption also via *in situ* XRD.

5.2 Experimental Section

5.2.1 CoAPO-SBE Materials Preparation

Cobalt-rich SBE samples were synthesized be means of hydrothermal reactions following the procedures reported in Chapter 2.

5.2.2 XRD of CoAPO-SBE materials

Samples used in these experiments were prepared in tablet form using direct compression in a punch press machine. About 0.5 grams of as-synthesized CoAPO-SBE were compressed from powder under 1000, 2500 or 4000 psi. This procedure provided samples with uniform external surface in order to maximize the XRD intensity recovery. The SBE crystalline structure was preserved after the process as confirmed also by XRD (data presented in the next section).

Powder XRD patterns of Co-SBE were obtained using a Bruckner D8 Advance system in a Bragg-Brentano vertical goniometer configuration, operating at 40kV and 40 mA. The angular measurements were made with a (Theta/2Theta) of ± 0.0001 reproducibility, applying steps of 0.01° from 5° to 40° to get XRD profiles that could be accurately resolved by least squares methods. The X-ray radiation source was a ceramic XRD Cu anode tube type KFL C 2K of 2.2 kW with a long fine focus. The diffraction patterns resulted in high-quality XRD profiles suitable for initial mathematical treatment and corroborate the crystallinity of the as-synthesized material. XRD data were in agreement with that of SBE reported in the literature. The gathering of the *in situ* XRD profiles for the H⁺-CoAPO-SBE sample was performed using an Anton Paar HTK-1200N stage. To obtain a detemplated CoAPO-SBE sample, the as-synthesized material was treated at 623 K for 5 h under N₂ (99.99%, Praxair) flowing at a rate of 50 mL/min. The sample was mounted onto an alumina sample holder fitted with a temperature sensor. The same stage was employed to collect the *in situ* XRD data of H^+ -CoAPO-SBE during CO₂ adsorption at 298 K and 1 atm. For the adsorption experiments, CO₂ (99.99%, Praxair) was allowed into the chamber at flow at a rate of 50 mL/min.

5.3 Results and Discussion

5.3.1. XRD Powley Refinement of CoAPO-SBE

Figure 5.1 shows a photo of the as prepared the CoAPO-SBE tablets while Figure 5.2 shows the corresponding XRD data. The latter confirmed the presence of the SBE phase.



Figure 5.1 CoAPO-SBE tablets prepared under a pressure of up to 4000 psi.

In order to resolve the powder diffraction data in the absence of a structural model, the wholepowder pattern decomposition method (WPPD) or Pawley refinement was employed to produce the individual Bragg components [1, 2]. The WPPD method can refine the unit cell parameters and decompose the whole powder pattern into individual reflections in one step [3]. The computer program used to carry out the calculations was the Bruker DIFFRAC*plus* TOPAS[™] software.



0



Figure 5.3 XRD powder profiles of the CoAPO-SBE as-synthesize sample at 25 °C.

In order to resolve the powder diffraction data, the whole-powder pattern decomposition method (WPPD), proposed by Pawley was used to separates into individual Bragg components in the absence of a structural model [1, 2]. This WPPD method can refine the unit cell parameters and decompose the whole powder pattern into individual reflections in one step [3]. The computer program used to carry out the calculations was the Bruker DIFFRAC*plus* TOPAS[™] software.

Figure 5.4 shows the resulting fitting of the XRD powder profiles of the as-synthetized CoAPO-SBE for the tetragonal P4/mmm and I4/mmm space groups. The cell parameters, the cell volume and the standard deviations are contained in the Table 5.1. According to theese data, an acceptable pattern fit was obtained with either of the P4/mmm (Figure 5.4a) and I4/mmm (Figure 5.4b) space groups. However, a better fit that includes all peaks was obtained for the tetragonal P4/mmm space group and this evident in Figure 5.4(a). In addition, the refined profile did not include parameters associated with preferred orientation correction, which could influence and improve the mathematical calculations. These results suggest that the powder CoAPO-SBE sample tested for this purpose is a structure less symmetric than the one previously reported by Stucky and co-workers in single crystal form [5]. Experiments were also performed in an attempt to perform a structural refinement for detemplated CoAPO-SBE materials. Figure 5.5. shows a stack of XRD patterns gathered during *in situ* tests in dry nitrogen and also during CO₂ adsorption. There are significant changes in the structure after thermal treatment, particular those related with the disappearance of the peak [101] (ca. $2\theta = 5^{\circ}$).



Figure 5.4(a) Pawley refinement of the XRD data gathered for the as-synthesized CoAPO-SBE sample.



Figure 5.4(b) Pawley refinement of the XRD data gathered for the as-synthesized CoAPO-SBE sample.

Sample	a[Å]	b[Å]	c[Å]	$V[Å^3]$	Space Group
-					
Co-SBE*	19.065	19.065	27.594	9320.78	P4/nnc
CoAPO-SBE	20.6407 ± 0.003	20.6407 ±0.003	26.9298 ±0.005	11473.1 ±0.004	P4/mmm
CoAPO-SBE	20.4548 ±0.003	20.4548 ±0.003	26.9885 ±0.005	11291.9 ±0.004	I4/mmm

 Table 5.1 Cell parameters and cell volume calculated using resolved powder XRD patterns.

*Source: International Zeolite Association [4]



Figure 5.5 XRD powder profiles in for CoAPO-SBE samples during detemplation and CO₂ adsorption.

5.4 Conclusions

In the analysis of the structure refinement by Pawley fitting method, indicated that the structure of CoAPO-SBE in powder form, crystallizes in a tetragonal arrangement and display a P4/mmm space group. Also it was noted that the compression treatment of the sample to obtain a sample with homogeneous surface, essential for the development of the XRD experiment, probably could weaken the structure so that the refinement of the detemplated CoAPO-SBE was not completed.

5.5 References

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Chapter 6 Concluding remarks

The main purpose of this work was to contribute to the development of nontraditional detemplation techniques and produce a novel cobalt-rich nanoporous SBE type aluminophosphate material for possible application as a sorbent for separation of gases. First and foremost, it was demonstrated that increasing the aging time employed during the synthesis of the cobalt aluminophosphate CoAPO-SBE greatly affects the morphological, structural and textural properties of the material. Furthermore, by minimizing the impact of the detemplation process on the integrity of the framework, particularly when the framework contains a high concentration of transition metals (i.e., Co/Al~1), we were able to obtain a material with a micropore surface area of at least 600 m²/g. Although the structure of the detemplated CoAPO-SBE was irreversibly destroyed upon contact with atmospheric air, the opposite was observed in oxygen-free atmospheres, even in the presence of moisture.

A new strategy for mild detemplation consisting of coupled partial detemplation and solid state ion exchange (PD/SSIE) was applied to functionalize the SBE material despite its low stability. CoAPO-SBE was detemplated and Na⁺ or Li⁺ were successfully introduced as extraframework species. This method provided, for the first time, a way to increase the

basicity of a cobalt-rich aluminophosphate with multidimensional porous containing extraframework cations and with outstanding textural properties. In terms of CO_2 adsorption performance, the sodium exchanged CoAPO-SBE was by far the best sorbent in both the low and high partial pressure ranges, and for the selective uptake of CO_2 . The resulting adsorbents displayed CO_2 uptake capacities that compare well with those of other aluminophosphates.

Finally, these results should provide a basis for the development of future MeAPOs catalysts and adsorbents with multidimensional pure systems and containing high framework transition metal concentrations.

Appendix A

Evaluation of temperature and time in the CoAPO-SBE detemplation process

The purpose of these studies was to estimate the optimal temperature and time to efficiently remove the template while maintaining the structure of the material. The optimum temperature and time were 5 h and 350 °C, based one the highest value of surface area and the best morphological quality of the crystal.



Figure A.1 Surface area distribution and SEM micrographs for detemplated CoAPO-SBE samples as a function of temperature. Detemplation was performed in ultra high vacuum at 250, 300, 550 and 400 °C, respectively.



Figure A.2 Surface area distribution for detemplated CoAPO-SBE samples as a function of time. Detemplation was performed in ultra high vacuum at 350 °C.

Appendix B

Synthesis of CoAPO-SEB using microwave assisted heating

The CoAPO-SBE material synthesis using microwave hydrothermal (MH) process was explored with the intention of optimizing time, quality, and quantity for the cobaltaluminophosphate structure. Figure B.1 presents porosimetry and light microscope imaging data for CoAPO-SBE prepared via microwave hydrothermal (MH) process at two different aging times and a temperature of 150 °C reached using a ramping time of 7 °C/min. The power used in the experiments was 300 W (400-75%). Although some of the samples prepared by MH show small hexagonal crystals indicating the presence of the SBE phase, the detemplated materials surface area remained below the one reported previously for SBE materials prepared via conventional heating methods.



Figure B.1 Surface area distribution and photographs for as-synthesized CoAPO-SBE samples using microwave oven.