

Novel Titanium Silicate Porous Materials: Synthesis using Large Structure Directing Agents, Functionalization and Evaluation for Carbon Dioxide Adsorption-Based Applications

by

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Abstract

UPRM-5 is a flexible titanium silicate and nano-porous adsorbent modified for the selective removal of CO₂ from light gas mixtures. In this work, UPRM-5 was prepared using TPA and TBA cations as structure directing agents by synthesis methods employing convective and microwave heating. The materials were effectively detemplated and functionalized with Sr²⁺ cations. Characterization of the functionalized materials with XRD at temperatures ranging from 25-300°C showed that the UPRM-5 variants synthesized with TBA have better thermal stability than the variant synthesized with TPA. The ²⁹Si MAS NMR experiments suggest that this may be due to fewer amount of structural faulting. In fact, high temperature *in situ* ²⁹Si MAS NMR demonstrated instability of the Si environments with thermal contraction due to dehydration and further re-hydration in both materials. Indexing of the XRD patterns showed, however, orthorhombic phases of UPRM-5 that remained at high temperatures. Diffusion time constants for the adsorption of CO₂ and CH₄ were estimated by using a volumetric phenomenological transport model that was corrected for particle size polydispersity. At optimum activation temperatures the kinetic selectivity of CO₂ over CH₄ were of 41 and 30 for Sr²⁺-UPRM-5 (TBA) and (TPA), respectively. Test beds were also assembled at the NASA ARC and UPRM, to study the dynamic adsorption of CO₂ from a gas mixture. The efficiencies of the test beds were calculated to be 77% for Sr²⁺-UPRM-5 (TBA) and 65% for Sr²⁺-UPRM-5 (TPA), over a range of CO₂ concentrations of 500-10000 ppm. A linear driving force (LDF) model was used to describe the CO₂ concentrations at the exit of the bed. In terms of regeneration, thermal activation between adsorption cycles showed to be detrimental to the equilibrium and dynamic capacities when done in a consecutive fashion. Reducing the system pressure, on the other hand, appears to be sufficient to completely regenerate the adsorbents, which is a significant cost effective alternative.

Resumen

UPRM-5 es un titano silicato flexible y un adsorbente nano-poroso modificado para la remoción selectiva de CO₂ de mezcla de gases. En este trabajo, UPRM-5 se preparó usando cationes de TPA y de TBA como agentes directores de estructura mediante métodos de síntesis que emplean calor convectivo y de microondas. La remoción de la plantilla y la funcionalización con cationes Sr²⁺ se realizó de forma efectiva. La caracterización con XRD a temperaturas de 25-300°C de los materiales funcionalizados, mostró que la variante de UPRM-5 sintetizada con TBA tiene mejor estabilidad termal que la variante sintetizada con TPA. Los experimentos de ²⁹Si MAS NMR sugieren que esto puede ser debido a una menor cantidad de fallas presentes en la estructura. Experimentos *in situ* a altas temperaturas de ²⁹Si MAS NMR demostraron la inestabilidad de los ambientes de Si en ambos materiales con la contracción de la estructura debido a la deshidratación y posteriormente, con la re-hidratación de la estructura. Indexado de los patrones de XRD mostraron fases ortorrómbicas de UPRM-5 que se conservaron aún a altas temperaturas. Constantes de tiempo de difusión para la adsorción de CO₂ y CH₄ se estimaron mediante el uso de un modelo de transporte fenomenológico volumétrico que se corrigió para polidispersidad en el tamaño de partícula. A temperaturas óptimas de activación las selectividades cinéticas de CO₂ sobre CH₄ son 41 y 30 para Sr²⁺-UPRM-5 (TBA) y (TPA), respectivamente. Lechos empacados de prueba para estudiar la adsorción dinámica de CO₂ en mezcla de gases se ensamblaron en el NASA ARC y el RUM. Las eficiencias de los lechos de pruebas fueron de 77% para Sr²⁺-UPRM-5 (TBA) y 65% y Sr²⁺-UPRM-5 (TPA), en un rango de concentraciones de CO₂ de 500 a 10000 ppm. Un modelo de fuerza de accionamiento lineal (LDF) se utilizó para describir las concentraciones de CO₂ a la salida del lecho. En cuanto a la regeneración, el tratamiento termal entre ciclos de adsorción mostró ser perjudicial para la capacidad de adsorción dinámica y en equilibrio cuando se hace de manera consecutiva. La reducción de la presión del sistema, por otro lado, parece ser suficiente para regenerar completamente los adsorbentes, lo cual constituye una alternativa más costo-efectiva.

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Dedication

DEDICATED TO MY PARENTS,

David Marcano Delgado and Sonia Noemi González Vives,

TO MY BROTHER,

Davidson Marcano González

AND TO THE REST OF MY FAMILY AND FRIENDS.

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Chapter 1

Introduction

1.1 Background

The “Gaia Hypothesis” first proposed by Lovelock and Margulis establishes, among other statements, that all living organisms behave as a super-organism capable of tuning climate by controlling the atmospheric chemical composition for its own benefit.¹⁻³ This hypothesis has produced great debate for the past 30 years, mainly as to whether or not this is a subject of life capability for environmental optimization, or just the observation of a feedback mechanism between the living and the lifeless matter.⁴ However, regardless of the basis of this relationship, the real problem seems to arise when the changes in the atmosphere are forced to occur on a rapid pace. The atmosphere, like most things in nature, can become unable to reverse or either adapt to the damaging effects of earth’s activities.

Global warming and climate change have been identified as the most critical of these effects and have been directly linked to anthropogenic greenhouse gas emissions accumulated in the atmosphere.⁵⁻⁷ The rapid increase in CO₂ emissions suggests that the atmospheric concentration levels will ramp up to 450 ppm by 2030, and to anywhere between 750 ppm to 1300 ppm by 2100.^{5, 6, 8} Since adverse climate change may endanger life sustainability, many measures had been taken in a worldwide effort to mitigate the effects of CO₂ in the atmosphere. One of these endeavors is direct minimization of CO₂ emissions, which, in most cases refers to the reduction of fossil fuels utilization. It has been found that about 78% of the greenhouse gas emissions from 2000-2010 came from fossil fuels combustion and industrial processes, the same contribution observed between the years 1970 and 2000.⁸ The problem arises in that the infrastructure of most countries

in the world is based on the use fossil fuels. In fact, it is predicted that with the current population growth in major cities around the globe, the energy consumption will double between 2010 and 2050.⁶ Given this scenario, other alternatives are continuously being evaluated to overcome the imminent effects of global warming.

In this regard, natural gas has been proposed as a primary step in reducing the use of other fossil fuels such as oil and coal, which are larger CO₂ emission contributors in comparison.¹⁰⁻¹² However, significant amounts of H₂S, N₂, in addition to CO₂ could make its efficiency as an energy source lower than that of petroleum-based fuels. The removal of these species from natural gas effluents makes it also a less cost-effective alternative, as the most common purification methods involve physical absorption of CO₂ with a solvent and this requires a substantial energy input during the regeneration stages. Other alternatives include cryogenic methods, which could achieve acceptable removal efficiencies but are also energy intensive.¹³⁻¹⁶

The selective removal of CO₂ via adsorption processes at or near-ambient conditions could be an attractive solution because of its effectiveness over large range of CO₂ concentrations and with minimum energy consumption. Yet, many of the available adsorbent materials still possess low working capacities. The design and production of adsorbents with framework properties that permit larger saturation capacities while sustaining the selectivity features may be a solution. Furthermore, these characteristics could make the said materials suitable for closed-volume applications in which atmospheric control or revitalization is required. Examples include spacecraft cabins and submarines in which breathable air require ultra-low carbon dioxide concentrations.^{17, 18} If not removed properly, the CO₂ produced by crewmembers can reach concentrations levels that can cause health problems such as headaches, visual disturbance and even hyperventilation, compromising the safety of a mission.^{19, 20}

The main challenge is to find inorganic adsorbent compositions that will permit an increase in micropore surface area while allowing surface tailoring and modulation of the dimensions of the pore entrance. Based on these aspects, a wide variety of adsorbents have been developed and found useful for multiple applications. Still, many efforts directed to the study and design of new adsorbents continue today, as well as improvements to adsorption processes and technologies. This chapter is intended to introduce, among other things, a novel adsorbent known as UPRM-5, the material of focus in this study for the prospective use in CO₂ adsorption based applications. It starts by describing the adsorption phenomena and the field of flexible titanium silicates. The justification, the objectives and an overview of this work are also presented.

1.1.1. Brief Introduction to the Adsorption Phenomena

The adsorption phenomenon is a mass transfer process that takes place when molecules, atoms or ions adhere to an interface (see Figure 1.1).²¹ Attachment of these is directly linked to the surface potential of the adsorbent material. An interaction potential arises when the bonding requirements (ionic, covalent or metallic) on the atoms conforming the adsorbent structure are fulfilled with others extra-framework atoms. These extra-framework species are not saturated, being rendered accessible as adsorption sites.²² The strength of the interactions can be classified in two ways: physisorption (mainly occurring due to non-specific dispersion, repulsion energies and electrostatic interactions) and chemisorption (related to complex formation and new bonds).²³ Physisorption is often preferred in most applications because it allows regeneration and reuse of adsorbents without large energy inputs.²⁴

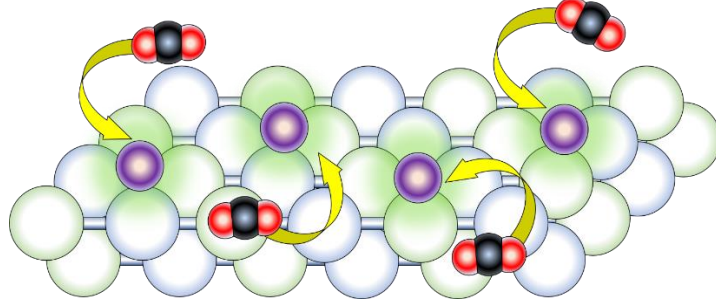


Figure 1.1 Illustration of an adsorbent surface. The purple spheres represent the adsorption sites and the surface potential. The adsorbates are represented by red/black molecules.

The potential adsorption energy describing the adsorbent-adsorbate interactions in the physisorption range, at ambient temperatures and low sorbate partial pressures is defined as follow:

$$\phi = \phi_D + \phi_R + \phi_{Ind} + \phi_{F\mu} + \phi_{\dot{F}Q} \quad (1.1)$$

This potential is associated to non-specific interactions (dispersion - ϕ_D and repulsion - ϕ_R), which depends on the polarizability of the molecules. The rest of the contributions are specific to the adsorbent surface electric field: ϕ_{Ind} is the interaction energy of the surface ion's electric field and a point dipole, $\phi_{F\mu}$ is the interaction between the electric field F and a permanent adsorbate dipole μ , and $\phi_{\dot{F}Q}$ is the interaction between the ion electric field gradient $\dot{F}$ and the adsorbate quadrupole moment Q .^{23, 25} These are all electrostatic interactions which can be expressed as follow:

$$\phi_{Ind} = -\frac{\alpha q^2}{2r^4(4\pi\epsilon_0)^2} \quad (1.2) \quad \phi_{F\mu} = -\frac{q\mu\cos\theta}{r^2(4\pi\epsilon_0)} \quad (1.3) \quad \phi_{\dot{F}Q} = -\frac{Qq(3\cos^2\theta-1)}{4r^3(4\pi\epsilon_0)} \quad (1.4)$$

where α is the polarizability, q is the electronic charge of the ion on the surface, ϵ_0 is the permittivity of a vacuum, μ is the permanent dipole moment, θ is the angle between the direction of the field or field gradient and the axis of the dipole or linear quadrupole, Q is the linear quadrupole moment, and r is the distance between the centers of the interacting species (i.e., ion or adsorption site and CO_2).

Table 1.1 shows the kinetic diameters, polarizabilities and quadrupole moments of three of the gases considered in this study. As observed, CO₂ has a significant advantage in terms of the contribution to the potential adsorption energy that imparts its quadrupole moment. In contact with an electric field on the surface of an adsorbent, CO₂ will be then selectively adsorbed over N₂ and CH₄. As expected from the interaction potentials described above, surface modification through ion functionalization –using ion-exchange techniques- may result in enhanced levels of adsorbate-adsorbent interactions and adsorption loadings, as more extra-framework cations with larger interaction potentials are incorporated in the sorbent’s surface.²⁶ Superior adsorbate-adsorbent interactions as well as a large adsorbent’s surface area are key factors to determine the best adsorbent choice. In fact, these factors will define the efficiency of the adsorption technology used for a desired application.^{23, 25}

Table 1.1 Kinetic diameters, polarizabilities, and quadrupole moments for CO₂, N₂ and CH₄.

Sorbate	Kinetic Diameter (Å)	Polarizability (cm³ × 10²⁵)	Quadrupole Moment (erg^{1/2} cm^{5/2} × 10²⁶)
 CO₂	3.30	29.1	4.3
 N₂	3.46	17.6	1.47
 CH₄	3.80	25	0

Gas adsorption applications are mainly directed to bulk separation and purification of gas mixtures. Adsorption separation processes are also mainly driven by steric, equilibrium and kinetic effects. Steric effects take place when the adsorbent pore opening is sufficiently small or partially blocked,

so that it will only allow the entrance of smaller molecules and exclude those larger than its size, i.e. molecular sieving. The equilibrium mechanism is related to the selectivity of the material towards certain adsorbate and its predilection to accommodate certain molecules at the adsorption sites. On the other hand, kinetic separations are mainly driven by differences in diffusional rates.²³ A combination of these effects can be obtained when using certain adsorbents and is often desirable for adsorbate-selectivity purposes.

The reach of the adsorption technology has proven to go as far as new adsorbents are design, characterized and modify for a specific application. Given the considerations mentioned above, a bottom-up design approach is preferable and has proved to be more efficient since the “heart” of any adsorption separation system is the adsorbent.^{27, 28} This, along with adsorption performance testing, is especially important for large-scale use of the adsorbents and their possible implementation cyclic processes, such as the temperature-swing adsorption and pressure-swing adsorption processes.¹⁷

1.1.2. Flexible Titanium Silicates

As previously suggested, an adsorption process directed for CO₂ removal should have good working capacity, selectivity, high diffusional rates and ease of regeneration with low energy requirements. Certain adsorbents have proved to excel in one or more of these aspects. Among them, there are zeolites, alumina, and mesoporous silica, all used commercially. Other recently studied porous adsorbents intended to work for CO₂ removal are aluminophosphates (AlPOs), silicoaluminophosphates (SAPOs) and, metal-organic frameworks (MOFs).^{23, 25, 28}

Titanium silicates adsorbents have also shown an outstanding potential for CO₂ removal applications. In their beginnings, titanosilicates were obtained essentially by substituting Al- with Ti- in the alumino-silicate crystal structure of common zeolites. One of this cases is TS-1, with a

structure similar to that of zeolite ZSM-5.²⁹ TS-1 was followed later by TS-2, with a MEL topology.³⁰ Finally, Engelhard Corporation developed the ETS titanium silicates series.³¹ Among them, ETS-4 and ETS-10 have become the most relevant, studied and modified for multiple applications, which ranges from gas separations to photocatalytic reactions and even the removal of Pb^+ from water.³²⁻³⁸

ETS materials are zeolite-like with octahedral and tetrahedral coordination units. ETS-4 exhibits a combination of titanium centers with semi-octahedral coordination states in the form of random faulting (see Figure 1.2), which allows the structure to be flexible upon dehydration while allowing for cation exchange (i.e., effective surface functionalization).^{31, 39, 40} This property allows for tuning of the pores, granting the capacity of gas separation due steric effects which becomes very useful in the separation of similar size gas molecules such as CO_2 , N_2 and CH_4 (see Table 1.1).^{31,}

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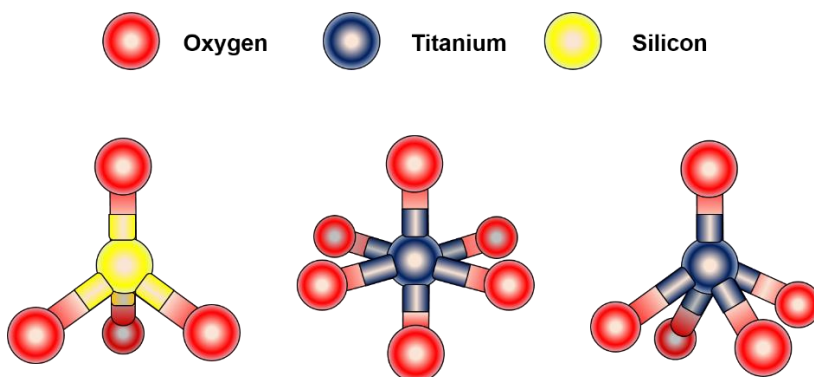


Figure 1.2 Flexible Titanium Silicates Framework's Structural Units

1.1.3. UPRM-5

In contrast with previously developed flexible titanasilicates (such as ETS-4³¹), UPRM-5 was first synthesized by Hernández-Maldonado and co-workers by employing tetraethylammonium (TEA) cations during the synthesis. These cations act as a structure-directing agent (SDA) by controlling, among other things, the pore channel geometry and dimensions of the adsorbent matrix. Compared

to ETS-4, the use of a template in the preparation of UPRM-5 gives it better thermal stability and a larger adsorption capacity without compromising the thermal pore contraction property (see Figure 1.3).^{31, 41, 42}

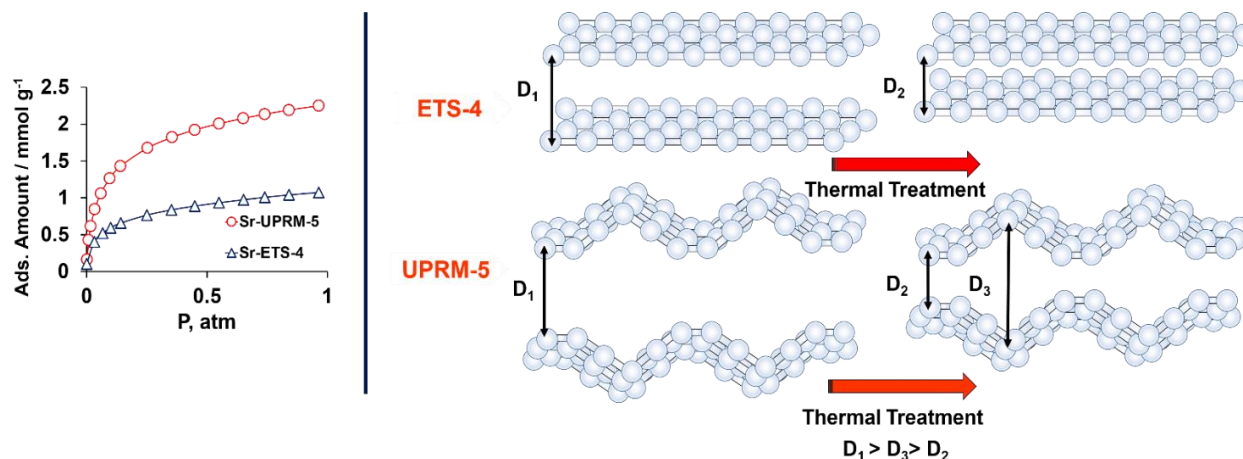


Figure 1.3 Adsorption Isotherms of Sr²⁺-UPRM-5 and Sr²⁺-UPRM-5. The illustration at the right shows how with thermal treatment UPRM-5 has a higher adsorption capacity than ETS-4. This is mainly because of the voids caused by the inclusion of SDAs in the synthesis of UPRM-5.

1.2 Justification

The implementation of synthesis strategies targeted to a specific objective can produce adsorbents with framework properties that permit larger saturation capacities while sustaining selectivity features. In the case of UPRM-5, evidence suggests that the use of an SDA controls the framework dimensions and the types of titanium coordination including those related to structural framework flexibility.^{41, 43} This could help in the design of materials with enhanced structural and textural characteristics, intended to address the great challenge of removing of CO₂ of light gas mixtures.

This thesis presents the characterization of UPRM-5 materials synthesized with larger NR₄ cations, tetrapropylammonium (TPA) and tetrabutylammonium (TBA), used as SDAs (see Figure 1.4). In addition, the potential of these materials for the kinetic separation of CO₂/CH₄ is shown as well as a thorough study of thermal contraction in both materials. Finally, re-activation procedures and

dynamic as well as transient performance tests for the removal of CO₂ were evaluated to determine the potential of these adsorbents for their integration in cyclic adsorption processes at large scale (i.e., natural gas purification, life support systems, etc.).

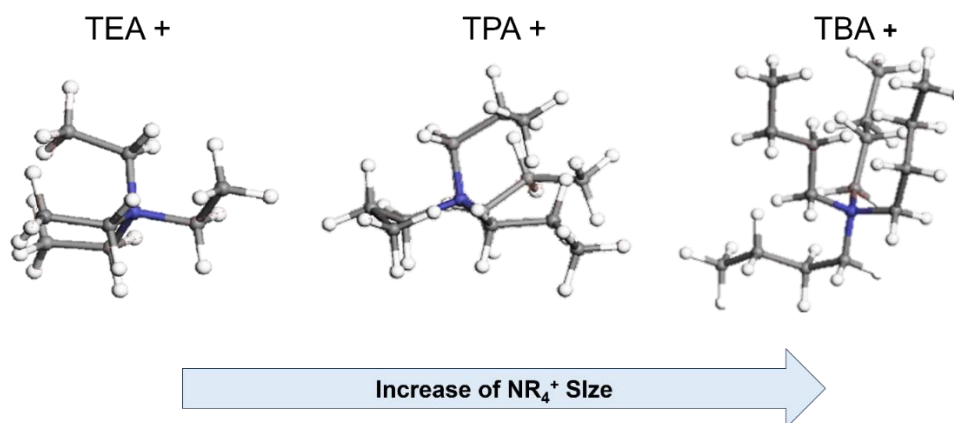


Figure 1.4 NR₄⁺ cations used as SDAs in the synthesis of UPRM-5.

1.3 Objectives

The overall objective of this work is the synthesis and characterization of UPRM-5 with larger quaternary ammonium cations, including (TPA) and (TBA), to establish a correlation between SDA type, size and framework coordination, and performance studies of the selective removal of carbon dioxide from light gas mixtures. The following are the specific objectives:

1.3.1. Synthesis, detemplation and functionalization of UPRM-5 titanium silicate porous sorbents with (TPA) and (TBA) as SDAs.

- Synthesis of the UPRM-5 framework via templated route with larger SDAs such as TPA and TBA.
- Fast UPRM-5 hydrothermal synthesis via microwave-assisted methods.
- Removal of the SDAs employing a non-destructive detemplation process.
- Effective functionalization of the detemplated material with extra-framework strontium (Sr²⁺) cations incorporated via liquid phase ion exchange.

1.3.2 Characterization of the Materials

- Determination of as-synthesized sample crystallinity and unit cell determination from X-ray diffraction (XRD) data.
- Assessment of sample purity, morphology and crystal size by means of scanning electron microscopy (SEM).
- Evaluation of the effect of detemplation and Sr^{2+} ion exchange on the integrity and coordination states of the UPRM-5 structure via XRD, ^{29}Si magic angle spinning nuclear magnetic resonance (MAS NMR) and Fourier transform infrared (FTIR) spectroscopy.
- Liquid nitrogen porosimetry testing to estimate textural properties such as micro pore and external surface area.
- Study of the thermally induced contraction process.
 - Evaluation of thermal stability via *in situ* high temperature XRD in combination with TGA.
 - Cautious indexing of the *in situ* XRD patterns to determine the long range structural changes involving contraction and expansion at high temperatures.
 - *In situ* ^{29}Si magic angle spinning nuclear magnetic resonance (MAS NMR) experiments for detection and characterization of the titanium coordination states upon thermal treatment.

1.3.3 Performance Tests

- Measurement and evaluation of CO_2 , CH_4 and N_2 pure component adsorption isotherms at different temperatures and for different adsorbent pre-activation temperatures.

- Estimation of isosteric heats of adsorption for CO₂ on Sr²⁺ exchanged UPRM-5 variants in order to elucidate the level of interactions between the adsorbate and the cationic species and describe the level of surface heterogeneity.
- Evaluation of a phenomenological transport model for the determination of diffusion time constants from fractional uptakes of CO₂ and CH₄ at different activation temperatures.
- Collection of CO₂ dynamic adsorption data by means of dynamic column break-through methods.
 - Analysis of the breakthrough curves to determine the adsorption capacity at the breakthrough point.
 - A study of the effects of flow velocity, gas feed concentration, bed size, and regeneration temperature on the adsorption capability of the materials.
 - Estimation of bed use efficiency through analysis of the adsorption capacities estimated from the breakthrough curves and the equilibrium data obtained via static volumetric adsorption experiments.
 - Simulation of breakthrough curves for fixed-bed adsorption and further comparison with experimental results.
 - Investigation of effective re-activation procedures between adsorption cycles involving thermal treatment.

1.4 Thesis Overview

The global objective of this dissertation was the synthesis and characterization of the UPRM-5 variants prepared using TPA and TBA. Equilibrium, kinetic and dynamic adsorption performance tests were also performed to evaluate the potential of these materials in the selective removal of CO₂ from light gas mixtures.

In Chapter 2 of this thesis, we have used TPA and TBA as structure directing agents for the synthesis of UPRM-5. The local-range structural characteristics were determined using ^{29}Si MAS NMR spectroscopy to evaluate the differences between the silicon environments of the as-synthesized materials. The materials were effectively detemplated and functionalized with Sr^{2+} cations. The pore contraction and thermal stability were assessed by means of *in situ* XRD and nitrogen porosimetry. Carbon dioxide loadings at equilibrium were measured for both, Sr^{2+} -UPRM-5 (TPA) and Sr^{2+} -UPRM-5 (TBA) in order to evaluate their adsorption performance at different activation temperatures and how this relates with the choice of SDA. Isosteric heats of adsorption measurements were also performed to determine surface properties of both UPRM-5 variants.

Chapter 3 aims to understand the thermally induced structural changes in Sr^{2+} -UPRM-5 variants prepared with TPA and TBA and their correlation to the diffusion of CO_2 and CH_4 at 25°C . *In situ* XRD patterns were indexed to determine the long-range structural changes that arise with thermal contraction. Meanwhile, *in situ* ^{29}Si MAS NMR was used to determine the short-range structural characteristics regarding the changes in the Si coordination environments with thermal treatment. A phenomenological volumetric transport model corrected for particle size polydispersity was used to estimate diffusion constants at 25°C in adsorbents pre-activated at different temperatures. Kinetic selectivity values for CO_2 over CH_4 were calculated to determine the potential of these materials to perform kinetic-based separations.

Chapter 4 presents a study of thermal re-activation between cycles and the effect in the adsorption working capacities obtained under dynamic and equilibrium conditions when done in a consecutive fashion. Sr^{2+} -UPRM-5 (TPA) and Sr^{2+} -UPRM-5 (TBA) beds were assembled to study CO_2 dynamic adsorption performance from N_2 . Measurements of bed usage efficiency were done

through the use of the Mass Transfer Zone model. Finally, a linear driving force (LDF) mass transfer rate model was used in the modeling of the bed outlet CO₂ concentration curves to describe the adsorption phenomena. The results of this assessment were used to evaluate their potential for CO₂ removal from close volume environments.

Some final remarks on the most relevant contributions and conclusions are presented in Chapter 5.

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Chapter 2

UPRM-5 Titanium Silicates Prepared Using Tetrapropylammonium and Tetrabutylammonium Cations: Framework Stability, Textural Properties, and Carbon Dioxide Adsorption

2.1 Chapter Summary

UPRM-5 is a flexible titanium silicate first prepared using tetraethylammonium (TEA) at exhibited improved structural and adsorption properties when compared to other titanium silicates. In order to further tailor these properties, we have employed tetrapropylammonium (TPA) and tetrabutylammonium (TBA), as structure directing agents (SDAs). Analysis of the local range structure using ^{29}Si magic angle spinning nuclear magnetic resonance spectroscopy suggested silicon environments corresponding to $\text{Si}(2\text{Si}, 2\text{Ti}_{\text{octa}})$ and $\text{Si}(3\text{Si}, 1\text{Ti}_{\text{semi-octa}})$, as expected for a flexible titanium silicate. A quantitative analysis, however, revealed that the amount of semi-octahedral titanium centers was greater in the variant prepared with TPA suggesting that the nature of the NR_4^+ cation plays an important role in the formation of framework faulting. Both UPRM-5 variants were detemplated and modified to include extra-framework Sr^{2+} and produce materials for carbon dioxide adsorption. Their thermal stability and pore contraction were first investigated by means of *in situ* high-temperature X-ray powder diffraction and nitrogen porosimetry. Materials prepared with TBA showcased better thermal stability when compared to variants prepared with TPA and even TEA, probably due to the relative low level of structural faulting. All variants, however, displayed a pore contraction process associated with the release of tenacious water. Carbon dioxide uptakes varied considerably depending on the choice of SDA employed and the isosteric heat of adsorption profiles correlated with a heterogeneous surface. The results suggest

that Sr^{2+} -UPRM-5 (TPA) materials could be tailored for purification applications, whereas Sr^{2+} -UPRM-5 (TBA) materials could be tailored for bulk-level separation applications.

2.2 Introduction

Titanosilicates with mixed octahedral–tetrahedral units have proved to be able to provide the necessary requirements to produce adsorbents for the deep removal of CO_2 . As mentioned in Chapter 1, flexible titanium silicate UPRM-5 was first synthesized using tetraethylammonium (TEA) cations as SDA^{1, 2}, resulting in a material with an enhanced thermal stability range and larger adsorption capacity without compromising the thermal pore contraction property.^{1, 2} However, there is still much more to learn about how the type and nature of the SDA controls the coordination of the titanium centers and the level of structural faulting that gives origin to the thermal flexibility of the framework.^{3, 4} Knowledge of this information would permit the design of more robust adsorbents to address the great challenge of reducing carbon dioxide emissions. In this chapter, we present the synthesis and characterization of UPRM-5 materials prepared with larger NR_4^+ cations [i.e., tetrapropylammonium (TPA) and tetrabutylammonium (TBA)] acting as SDAs. The as-prepared UPRM-5 variants (i.e., TPA- and TBA-UPRM-5) and their detemplated and strontium exchanged versions have been characterized here via powder X-ray diffraction (XRD), diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy, thermal gravimetric analysis (TGA), scanning electron microscopy (SEM), elemental analysis, and porosimetry techniques, to explain the structural properties relevant to the material adsorption performance.

In addition, *in situ* high-temperature XRD and ^{29}Si magic angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy data has been studied to understand the framework contraction process. Adsorption isotherms for carbon dioxide, methane, and nitrogen as well as carbon dioxide isosteric heat of adsorption on the Sr^{2+} variants are also shown.

2.3 Experimental Procedure

2.3.1 UPRM-5 microwave-assisted synthesis, detemplation, and functionalization

Syntheses under autogenous conditions were carried using microwave-assisted system (MARS-5, CEM Corporation). Two gel mixtures with the following composition were prepared for each of the SDAs used in this study: $3.4(\text{TBA})_2\text{O}:7.3\text{-Na}_2\text{O}:1.2\text{K}_2\text{O}:1.3\text{TiO}_2:10\text{SiO}_2:201\cdot5\text{H}_2\text{O}$; and $3.4(\text{TPA})_2\text{O}:7.3\text{Na}_2\text{O}:1.2\text{K}_2\text{O}:1.3\text{TiO}_2:10\text{SiO}_2:201\cdot5\text{H}_2\text{O}$. A portion of the mixtures was placed into 100-mL Teflon vessels (XP-1500 Plus, CEM Corporation). A control vessel also containing one of the said mixtures was used to avoid damaging of the MARS-5 optical fiber temperature probe and sapphire thermowell. This was accomplished by adjusting the pH to 7 with a 6 M HCl aqueous solution. The samples were heated to 215°C using a temperature ramp of 20°C min⁻¹. The reaction or aging time varied from 4 to 24 h at a power level that did not exceeded 400 W. The resulting solid materials (i.e., TPA- and TBA–UPRM-5) were recovered via vacuum filtration, washed with 2 L of distilled/deionized water and stored in a forced convection oven at 60 °C for 18 h. For carbon dioxide adsorption measurements, the samples were first detemplated via ion exchange with NH₄⁺ and followed by exchange with Sr²⁺ cations, using NH₄Cl and SrCl₂ aqueous solutions, respectively.

The ion-exchange procedures are described elsewhere.^{2, 5, 6} For clarity, the strontium exchanged samples will be labeled Sr²⁺–UPRM-5 (TPA) and Sr²⁺–UPRM-5 (TBA) depending on whether tetrapropylammonium or tetrabutylammonium cations were employed as SDAs, respectively.

2.3.2 Materials characterization

Standard XRD patterns of as-synthesized TPA– and TBA– UPRM-5 were obtained using a Rigaku Ultima III XRD unit fitted with cross beam optics, a Cu Kα target and calibrated for focusing-type optics. A voltage and current of 40 kV and 44 mA, respectively, was used for operation. Patterns

were collected for 2θ diffraction angles from 5° to 40° at a scanning rate and step size of 1° min^{-1} and 0.02° , respectively. SEM analysis of the samples was performed using a JEOL-JSM-6930LV scanning electron microscope operating at a voltage range of 5.0–20.0 kV. The images were obtained following standard procedures for low conductive samples. The SEM micrographs were employed to identify the morphology and estimate the average crystal size of UPRM-5 samples. Elemental analysis of the Sr^{2+} ion exchange materials for silicon, titanium, and strontium content was completed using inductively coupled plasma mass spectrometry. These tests were performed at Galbraith Laboratories, Inc., Knoxville, TN.

A high-resolution TA-Q500 system was used to perform TGA measurements under a constant helium flow of 60 mL min^{-1} and heating from room temperature to 600°C at a rate of 5°C min^{-1} . DRIFT spectra were acquired for all samples in the $600\text{--}4000 \text{ cm}^{-1}$ range with a resolution in absorbance of 4 cm^{-1} using a Nicolet 6700 Optical Spectrometer unit fitted with a Praying Mantis Diffuse Reflectance module (Harrick Scientific Products, Inc.). A DLa TGS detector was employed during the DRIFT measurements. *In situ* high-temperature XRD patterns of Sr^{2+} –UPRM-5 (TPA) and -UPRM-5 (TBA) variants were gathered using a high-temperature ReactorX module (Rigaku Corporation) attached to the aforementioned Rigaku Ultima III system. The module allows enclosure of the sample under a control environment while allowing the passage of X-rays by means of a continuous beryllium window. Precise *in situ* heating was accomplished by means of an infrared-based source. The sample is loaded into the ReactorX module by means of a black quartz plate that allows the attachment of a $1/1600$ diameter thermocouple for accurate temperature measurement. X-ray scans were gathered at $3.5^\circ \text{ min}^{-1}$ while the sample was heated from room temperature to 600°C at 1°C min^{-1} in flowing helium (Ultrahigh Purity Grade, Praxair) at 60 mL min^{-1} .

High-resolution solid-state ^{29}Si MAS NMR experiments for as-synthesized TPA–UPRM-5 and TBA–UPRM-5 were performed on a ultra-narrow bore 19.6 T magnet using a Bruker DRX NMR console with the ^{29}Si Larmor frequency of 165.55 MHz and using an in-house built 4-mm single resonance MAS NMR probe. A single 2- μs pulse ($\approx 15^\circ$ flip angle) was used to directly excite the ^{29}Si magnetization. The sample was spun at 8 kHz and 4096 transients were used to accumulate the signal with a recycle delay of 10 s. The ^{29}Si chemical shifts were referenced to 4,4- dimethyl-4-silapentanesulfonate sodium. No line broadening was used in the spectrum.

2.3.3 Textural properties, adsorption measurements, and isosteric heat of adsorption

Surface area measurements were done for Sr^{2+} –UPRM-5 (TPA) and Sr^{2+} –UPRM-5 (TBA) variants using a Micromeritics ASAP 2050 static volumetric adsorption system. Nitrogen volumetric equilibrium adsorption at -196°C was used to determine the adsorbent variants textural properties. Prior to each analysis, these samples were activated or degassed in vacuum at 90, 120, 150, 180, 240 or 300°C for 18 h. In addition, the resulting nitrogen adsorption isotherms were transformed using the t-plot method (Lippens and de Boer) to determine the micropore surface area.⁷⁻⁹ Pure component carbon dioxide adsorption analyses were also performed on the strontium ion-exchanged UPRM-5 variants, at 25°C and pressures up to 7 atm. The analyses were performed using the volumetric adsorption apparatus previously mentioned and carbon dioxide gas (Ultrahigh Purity grade, Praxair). Adsorbent activation (as described above) was also performed prior these analyses. In addition, the CO_2 equilibrium adsorption data with the Langmuir–Freundlich (L–F)^{10, 11} and Dubinin–Astakhov¹⁰ models. The L–F equation is given by:

$$\frac{q}{q_0} = \frac{(bP)^{1/n_{LF}}}{1+(bP)^{1/n_{LF}}} \quad (2.1)$$

while the D-A equation is given by:

$$\frac{q}{q_0} = \exp \left[- \left(C \ln \frac{P_s}{P} \right)^{n_{DA}} \right] \quad (2.2)$$

where C is defined by:

$$C = \frac{RT}{\beta E} \quad (2.3)$$

and q is the adsorbed amount, q_0 is the saturated adsorbed amount, b is an interaction parameter, P is the partial pressure, P_s is the saturated vapor pressure of the adsorbate, R is the universal ideal gas constant, T is the absolute temperature, β is the affinity coefficient, E is the characteristic adsorption energy, and the n_{LF} and n_{DA} are constants related to the surface heterogeneity. Saturated adsorbed amounts for carbon dioxide were estimated from the isotherms data gathered at 0°C and assumed constant during fitting of isotherm data gathered at other temperatures. This is a reasonable approach since sorbate-sorbate interactions become negligible at lower temperatures and loading saturation amounts could be achieved at a much lower pressure range. In addition, saturated vapor pressure data above the critical point were estimated using the reduced Kirchoff equation^{12, 13}.

Isosteric heats of adsorption of carbon dioxide onto the Sr^{2+} ion exchanged UPRM-5 variants were determined using the classic Clausius-Clapeyron equation at constant surface loading:

$$\left. \frac{d \ln P}{d (1/T)} \right|_{q=\text{const.}} = - \frac{\Delta H_{ads}}{R} \quad (2.4)$$

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

2.4 Results and Discussion

2.4.1 Materials synthesis and characterization

Microwave irradiation has been proven to be a useful method to reduce synthesis completion time due to a more efficient heating of reaction mixtures. Different from conventional convective heating, microwaves reduce the presence of second phases by increasing the synthesis crystallization rates.^{1, 14-16} Hernandez-Maldonado and co-workers have shown that neat crystals of UPRM-5 prepared with TEA as SDA can be obtained at 16 h through microwave irradiation, compared with 12 days using conventional hydrothermal conditions.^{1, 2} To optimize the synthesis reaction time for TPA– and TBA– UPRM-5, microwave-assisted synthesis were performed for time or aging periods between 4 and 24 h.

XRD patterns for as-synthesized TPA– and TBA– UPRM-5 as a function of synthesis time are gathered in Figures 2.1 and 2.2, respectively.

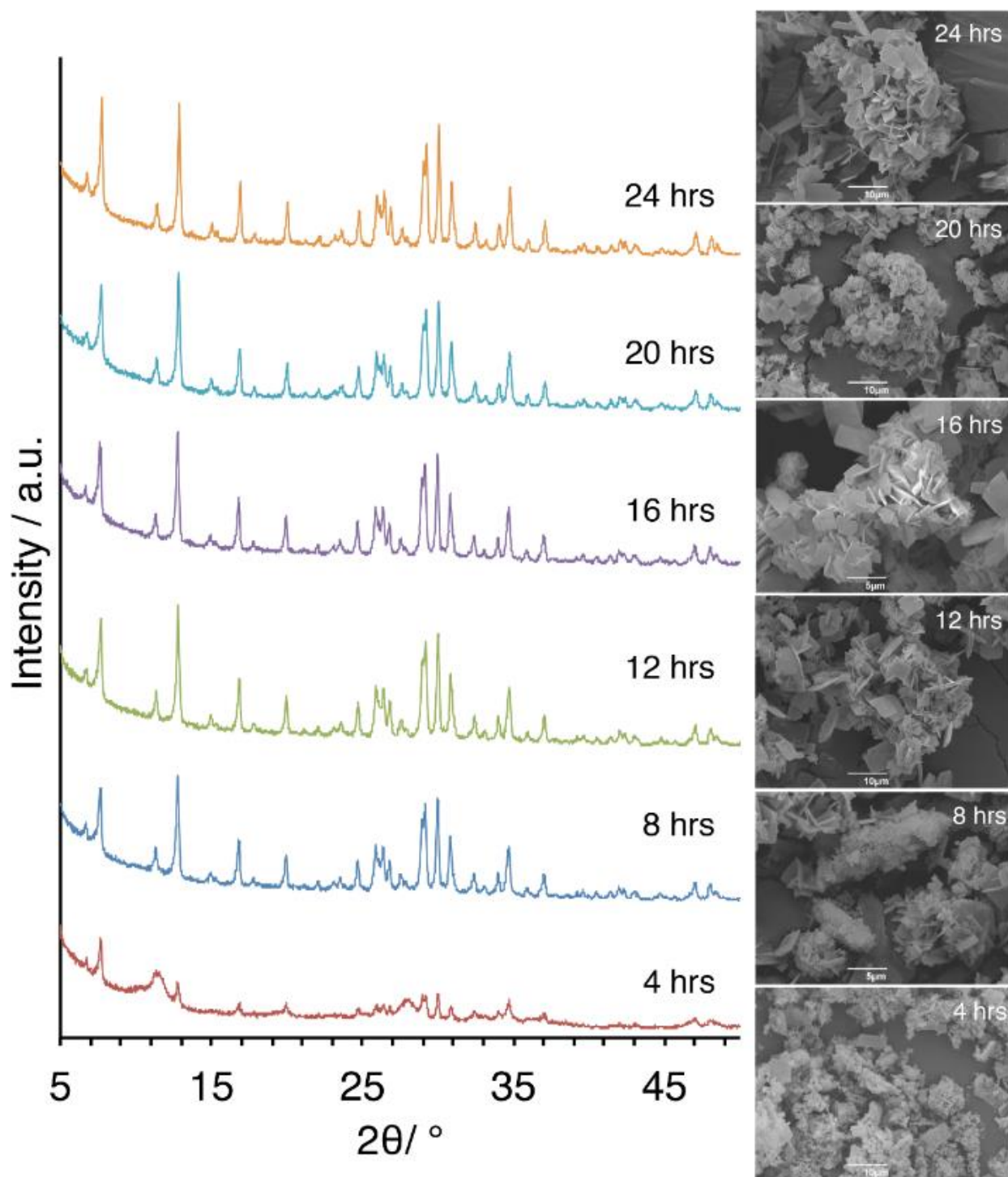


Figure 2.1 XRD patterns and SEM images of as-synthesized TPA-UPRM-5 materials prepared at different aging times and via microwave assisted heating.

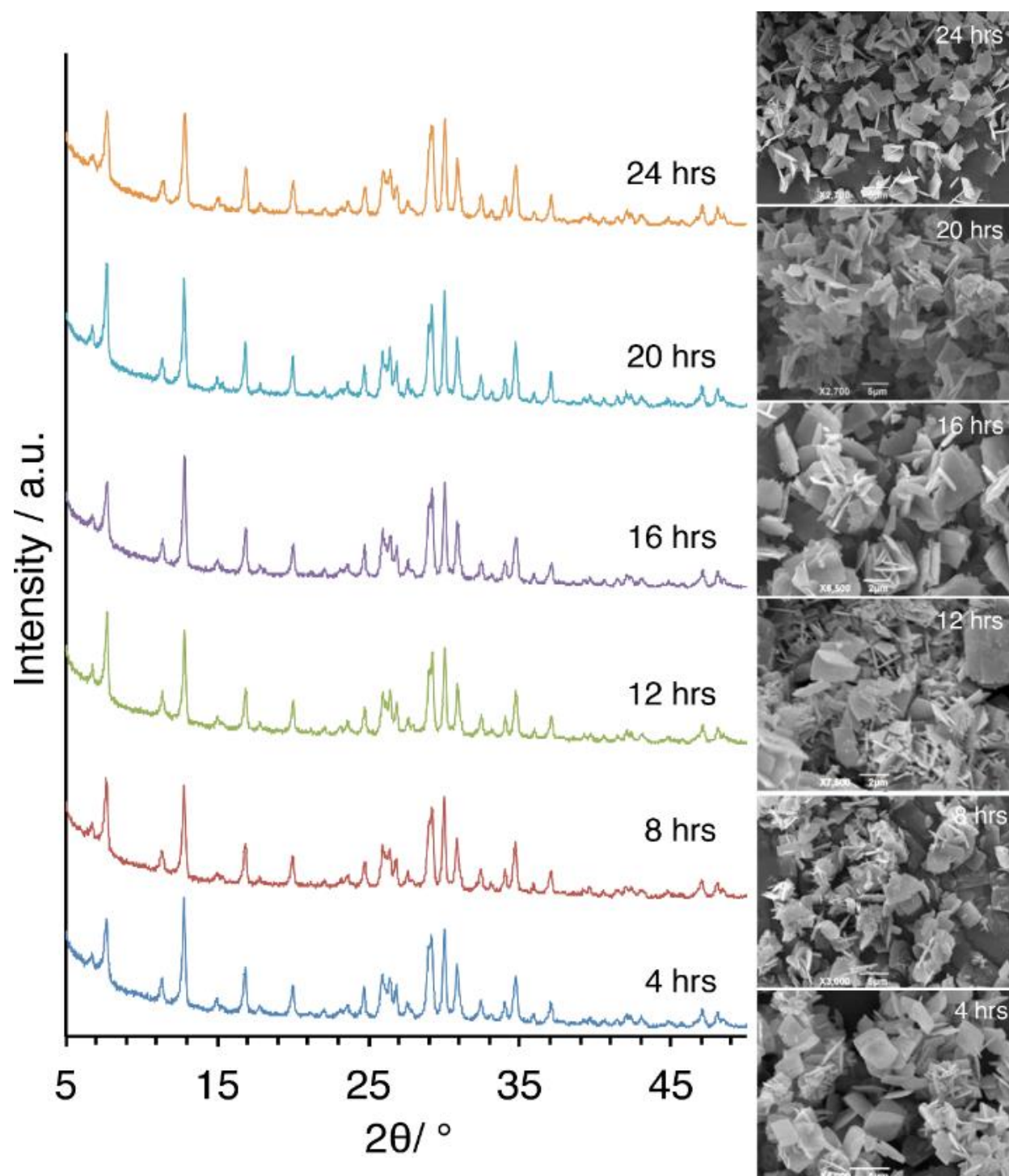


Figure 2.2 XRD patterns and SEM images of as-synthesized TBA-UPRM-5 materials prepared at different aging times and via microwave assisted heating.

According to the overall intensity peak profile, the sample with higher crystallinity corresponded to TPA–UPRM-5 synthesized at 24 h. However, the SEM micrographs showed that a pure UPRM-5 phase could be obtained after just 12 h. Using the same criteria, for TBA–UPRM-5 the highest crystallinity was obtained for a reaction time of 20 h. Rectangular TPA–UPRM-5 crystals are clearly seen after at least 12 h of reaction time. Shorter reactions times resulted in the presence of a secondary phase that appears to be mostly amorphous (see SEM micrographs in Figure 2.1). A similar behavior trend was observed during the synthesis of TBA–UPRM-5 (Figure 2.2). It is important to point out that even when both materials exhibited similar crystals or particle morphology, the ones corresponding to TPA–UPRM-5 are larger in size when compared to those TBA–UPRM-5. In fact, the average thickness of the crystals plates for TPA–UPRM-5 is nearly an order of magnitude larger than that of the other variant. Although this difference is plausibly attributed to the use of different SDAs^{3,4}, it could also be attributed to the different reaction times employed during the microwave-assisted heating synthesis.^{15, 17}

For titanosilicates ETS-10 and ETS-4, the XRD peaks observed in the $2\theta = 5\text{--}15^\circ$ region have been related to the octahedral and semi-octahedral titanium chains encompassing the pore channels.¹⁸⁻²¹ Assuming that both the UPRM-5 variants study here can be obtained by superposition of polymorphs which are also representative of the ETS-4 materials, the aforementioned XRD analysis could be employed for the data shown in Figures 2.1 and 2.2. The patterns exhibit relative intensities with maxima at 2θ equal to 7.6° for the samples prepared with TPA and 2θ equal to 12.6° for the ones prepared with TBA. Therefore, the differences in relative intensities in the 2θ equal to $5\text{--}15^\circ$ region may suggest different levels of faulting or amount of semi-octahedral titanium centers located near the pore rings. In order to verify this the samples were subjected to ^{29}Si MAS NMR tests.

According to the NMR spectra shown in Figure 2.3, each UPRM-5 variant exhibits two resonances (i.e., -93 and -97 ppm) and each could be related to silicon environments corresponding to $\text{Si}(2\text{Si}, 2\text{Ti}_{\text{octa}})$ and $\text{Si}(3\text{Si}, 1\text{Ti}_{\text{semi-octa}})$.^{1, 22-24} After careful spectral deconvolution, the resulting peak intensities of the MAS NMR resonances could be related to the concentration of the two different titanium coordination environments. In other words, the analysis would yield a ratio between the amounts of octahedrally coordinated titanium to the amount of semi-octahedrally coordinated titanium. For TPA- and TBA-UPRM-5, these ratios are 2.6 and 3.7, respectively, which may indicate that there is a higher amount of semi-octahedrally coordinated titanium in the samples prepared with TPA-. Combining these results with those observed in Figures 2.1 and 2.2, one may assume that the 2θ equal to 12.6° peak maximum intensity corresponded to a lower level of random framework faulting. Similar findings have been reported for ETS-4 materials.^{20, 22}

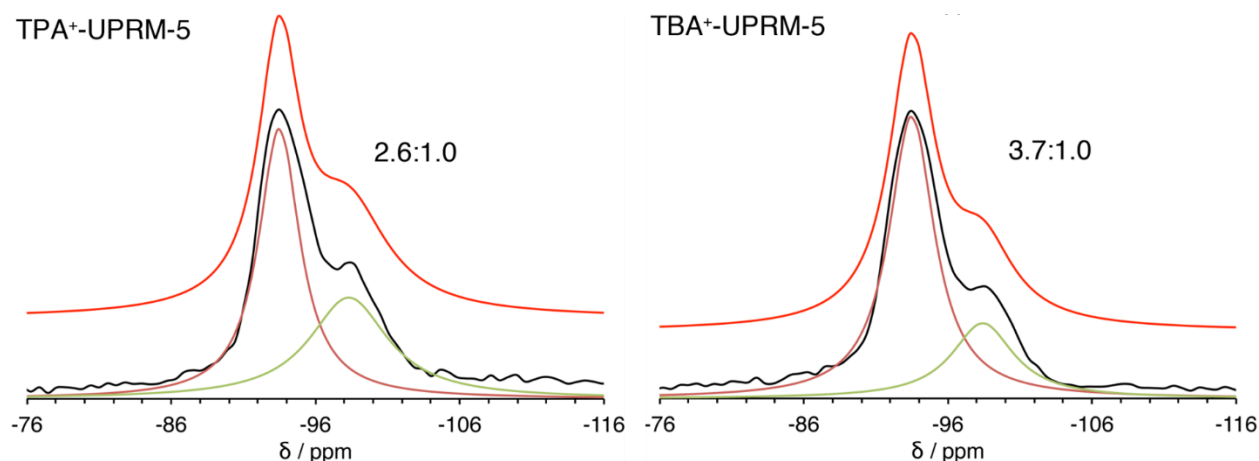


Figure 2.3 ^{29}Si MAS-NMR spectra for as synthesized TPA- and TBA-UPRM-5.

2.4.2 Material detemplation and strontium incorporation: DRIFT and TGA

The DRIFT technique was used to determine, in a qualitative fashion, the effectiveness of the ion exchange procedures both for the detemplation and effective functionalization of the material (Figure 2.4). The infrared spectra for both as-synthesized UPRM-5 variants displayed bands in the $1030\text{-}1060\text{ cm}^{-1}$ and $666\text{-}672\text{ cm}^{-1}$ regions and these were related to the skeletal NC_4 stretching

characteristic of quaternary ammonium cations and revealing the presence of the SDAs. The bands positioned at ca. 920 and 1000 cm^{-1} were related to the C-N stretching while the one located at ca. 1132 cm^{-1} was related to the C-N-C antisymmetric stretching, corroborating yet again the presence of the SDAs. The NH_4^+ exchanged samples showed bands in the 1400-1440 cm^{-1} and 2800-3500 cm^{-1} regions that were related to the ingoing cation. However, bands related to the SDA were not appreciable. For the Sr^{2+} ion-exchanged samples, none of the aforementioned spectral bands were present, confirming complete removal of the ammonium species. It should be mentioned that all samples exhibited DRIFT bands in the 650-1400 cm^{-1} region, but the intensity of these were much lower for the ion-exchanged variants. A similar result was obtained by Hernández-Maldonado and co-workers for a UPRM-5 materials prepared with TEA.¹ These bands correspond to the stretching of the TO_4 tetrahedra and not the template.^{25, 26}

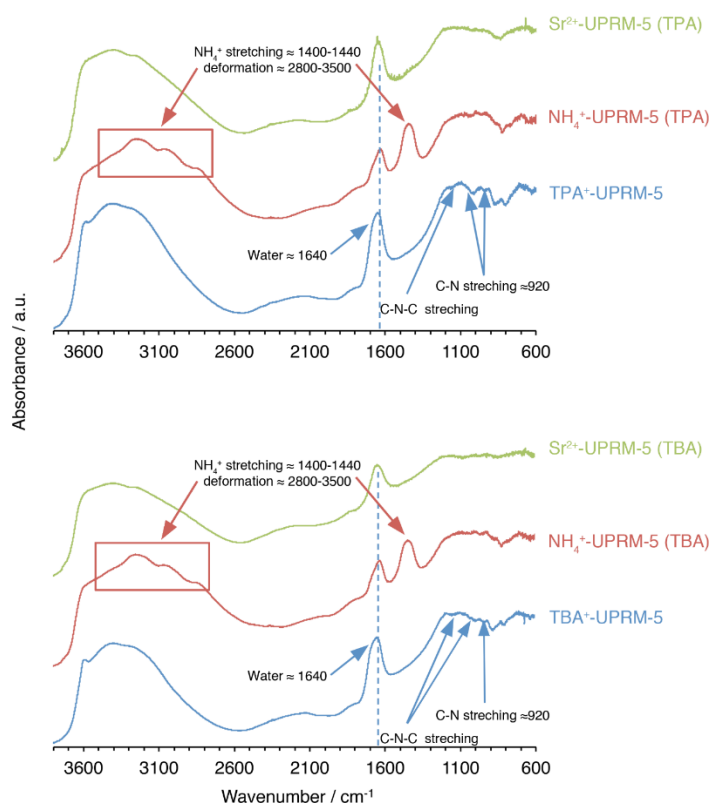


Figure 2.4 FT-IR spectra for as-synthesized and ion exchanged UPRM-5 materials.

Compositional data gathered from TGA results served as additional evidence for the effectiveness of the SDA removal procedure and further ion exchange (see Table 2.1). After ion exchange for Sr^{2+} , both of the UPRM-5 variants contained no SDA moieties. Instead, the samples contained for more loosely bound water molecules, probably occupying the now detemplated pores. However, it is worth noting that the amount of structural or tenacious water remained almost the same in all of the samples (both as-synthesized and ion exchanged). Such type of water has been linked to hydroxyl groups coordinated to semi-octahedral titanium in ETS-4 materials.¹⁹

Table 2.1 Structure directing agent (SDA) and water content estimated from TGA data.

Sample	SDA (wt.%)	Loosely Bound Water Content (wt.%)	Tenacious Water Content (wt.%)	Total Water Content (wt.%)
As synthesized TPA-UPRM-5	2	8	7	15
As synthesized TBA-UPRM-5	4	5	8	13
Sr^{2+} -UPRM-5 (TPA)	0	13	6.5	19.5
Sr^{2+} -UPRM-5 (TBA)	0	15	4.5	19.5

2.4.3 *In situ* high-temperature XRD

The long-range order of the Sr^{2+} ion exchanged UPRM-5 materials (i.e., Sr^{2+} -UPRM-5 (TPA) and Sr^{2+} -UPRM-5 (TBA)) frameworks was monitored during heat treatment *in situ* via XRD and the results are gathered in Figures 2.5 and 2.6. TGA profiles were also included in these figures to help in correlating any structural changes to the elimination of loosely and strongly bound water molecules. For Sr^{2+} -UPRM-5 (TPA), the *in situ* XRD patterns stack (Figure 2.5) showed several peaks shifting to higher diffraction angles (or lower d-spacing) after 90°C. Peak shifting was more significant in planes corresponding to ca. 2θ equal to 7.6, 12.7 and 20.0°. A similar observation can be made for the case of Sr^{2+} -UPRM-5 (TBA), with peaks displacement starting at temperatures

higher than 120°C. The aforementioned peaks could be associated to the materials pore system, in which faulting would be introduced by semi-octahedral titanium. Since stabilizing water molecules are directly correlated to these semi-octahedral species¹⁹, the observed peak shifts could be associated to the release of these tenacious water molecules and due to cation relocation.¹⁵ In the case of Sr²⁺-UPRM-5 (TBA), the structural changes due to the release of tenacious water became more evident at 210°C where a new peak appears at around 2θ equal to 13.8°. For ETS-4 materials, the position corresponding to this peak has been considered to be very sensitive to the dehydration process and apparently this is also the case for Sr²⁺-UPRM-5 (TBA). However, this reflection appears to fade off at higher temperatures probably as a result of pore distortion or blocking due to the framework contraction.¹⁹ Significant changes at higher temperatures and the resulting partial destruction of the structure in both UPRM-5 variants are also evident in Figures 2.5 and 2.6. The latter could be a result of the collapsing of the semi-octahedral titanium centers.^{15, 21} However, it is quite clear that the UPRM-5 variant that results from using TBA as the SDA possess a much higher thermal stability when compared to the one prepared with TPA. This finding matches well with the MAS NMR data discussed above, which indicates that the variant prepared with TBA contained less semi-octahedral titanium centers and, therefore, probable less structural faulting.

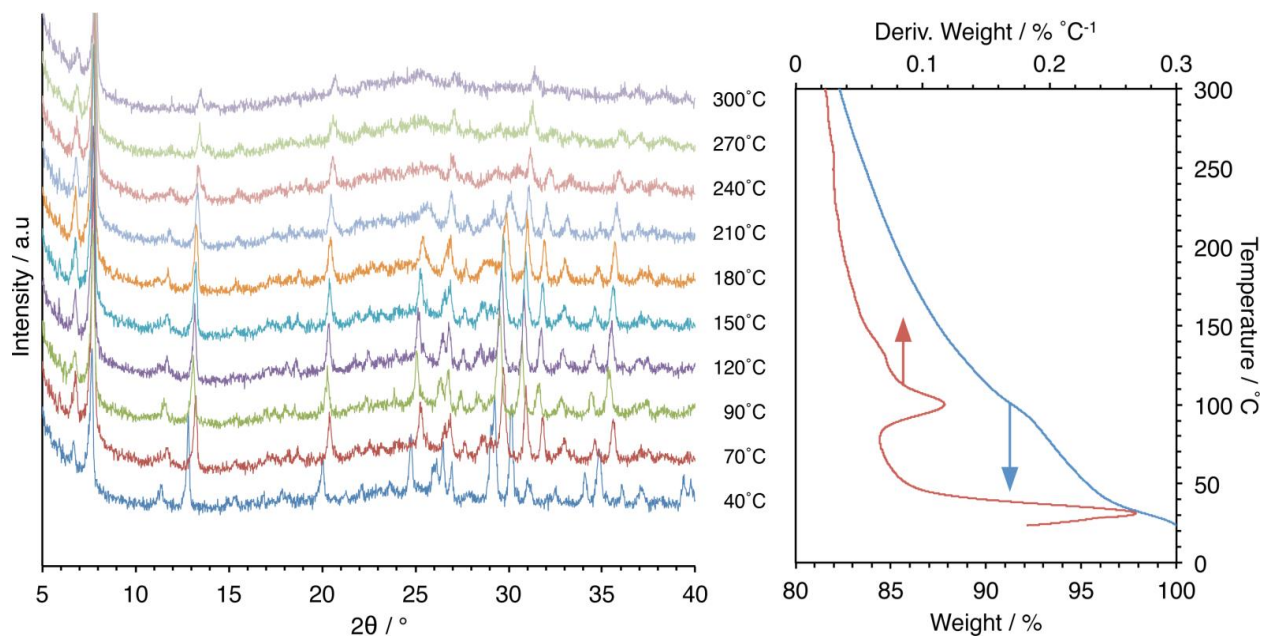


Figure 2.5 In situ high temperature XRD patterns and TGA profiles of Sr^{2+} -UPRM-5 (TPA) gathered under dry helium atmosphere.

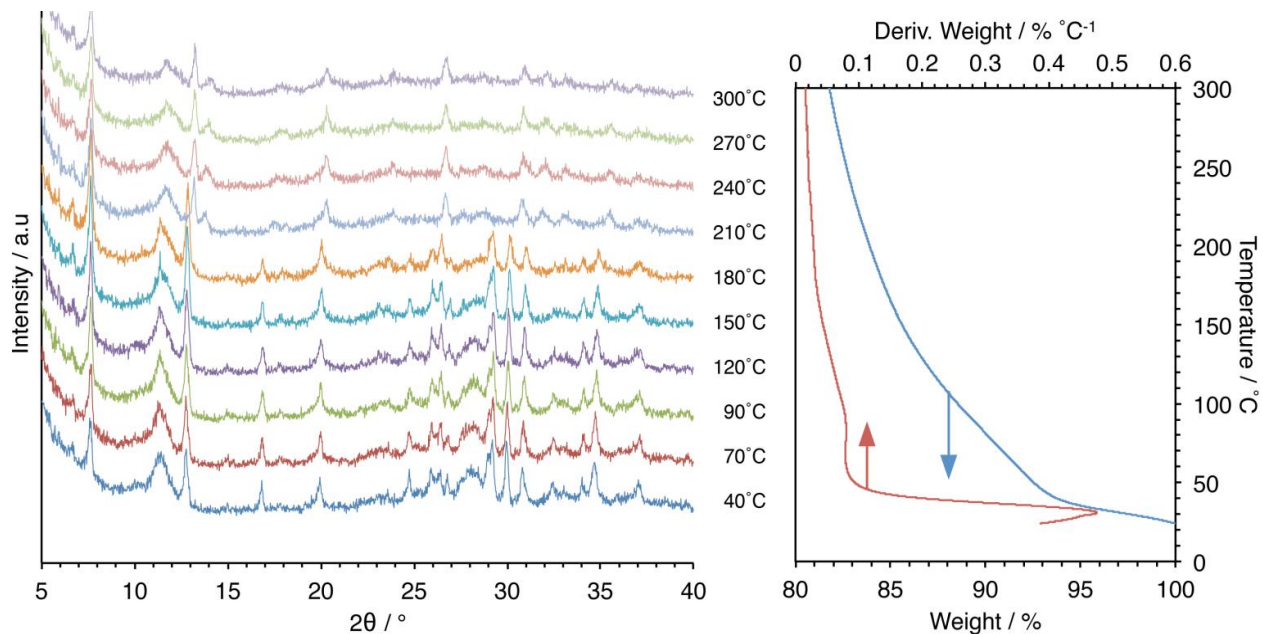


Figure 2.6 In situ high temperature XRD patterns and TGA profiles of Sr^{2+} -UPRM-5 (TBA) gathered under dry helium atmosphere.

Profiles of apparent crystallinity versus temperature were calculated based on the data obtained from the *in situ* XRD tests and these are gathered in Figure 2.7.

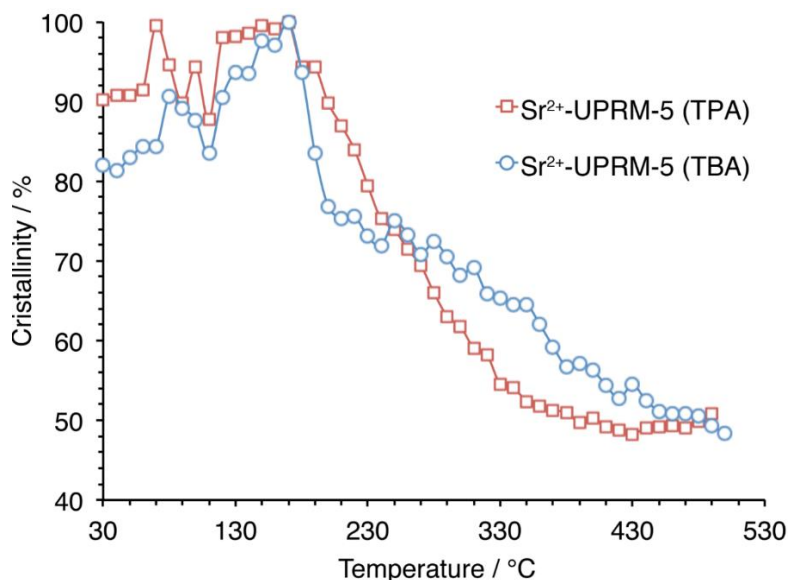


Figure 2.7 Crystallinity profiles of Sr^{2+} -UPRM-5 (TPA) and Sr^{2+} -UPRM-5 (TBA) samples during thermal treatment.

Both of the Sr^{2+} -UPRM-5 variants apparently achieved the highest crystallinity at 170°C. At temperatures higher than 350°C the crystallinity is reduced to almost 50% but remained constant. Partial conservation of the framework at these temperatures could be attributed to octahedral titanium centers remaining intact.²⁸

2.4.4 Surface Area Measurements

Different from ETS-4, UPRM-5 materials are able to maintain framework flexibility upon dehydration while sustaining larger adsorption capacities. This is reflected, for instance, in some of the textural properties of the UPRM-5 variants. Hernández-Maldonado and co-workers have shown that Sr^{2+} exchanged UPRM-5 materials originally prepared with TEA acting as a SDA has a surface area of 288 m² g⁻¹ after an activation or degassing temperature of 90°C and vacuum are employed.² In the present work, Sr^{2+} -UPRM-5 (TPA) and Sr^{2+} -UPRM-5 (TBA) showcased a

maximum surface area of 217 and 261 $\text{m}^2 \text{g}^{-1}$, respectively, after employing optimal activation temperatures (see Figure 2.8). Since these area values contain contributions from the particles external and microporous features that are coupled, it was necessary to further analyze the N_2 adsorption isotherms (-196°C) and quantify the effect of the thermal treatment on the external surface and pore individually (i.e., decoupling). This was accomplished via a t-plot analysis method^{3, 6, 7} and the results are also shown in Figure 2.8.

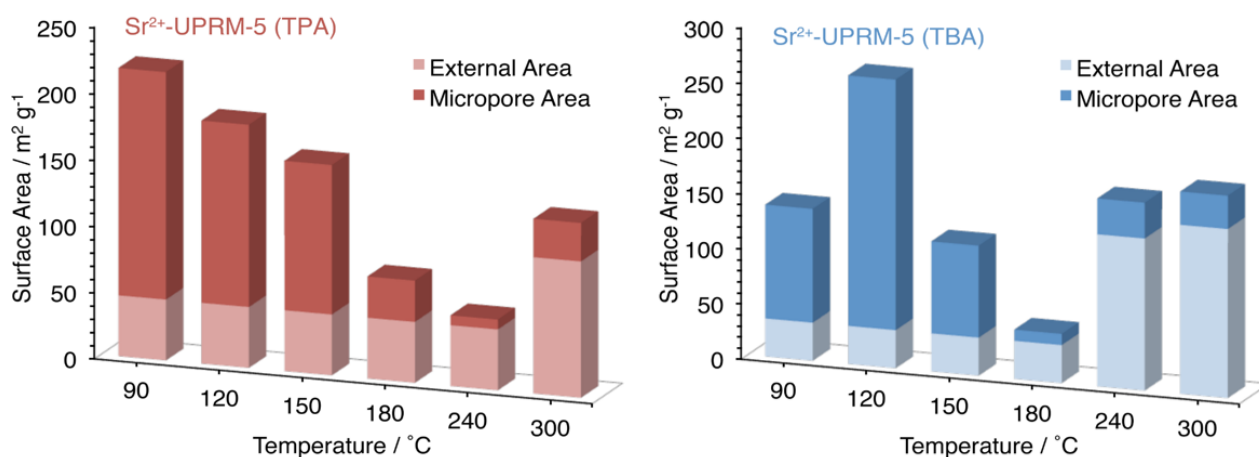


Figure 2.8 Surface area distribution for Sr^{2+} -UPRM-5 (TPA) and Sr^{2+} -UPRM-5 (TBA) samples activated at different temperatures.

Upon thermal treatment in vacuum, the Sr^{2+} -UPRM-5 (TPA) material external surface area remained nearly constant up to a temperature of ca. 240°C (see Figure 2.8). This translates to pore shrinkage or distortion upon thermal treatment. Upon reaching a temperature of around 300°C the external surface area increases considerably, indicating destruction of the structure and matching the results obtained from the *in situ* high temperature XRD analyses (see Figure 2.5). In the case of Sr^{2+} -UPRM-5 (TBA), the external surface area increases at a much lower activation temperature when compared to the UPRM-5 variant prepared with TPA. In fact, SEM micrographs (see Figure 2.9 and Figure 2.10) obtained for samples treated at the aforementioned temperature showed particle macro scale fractures, which could explain the sudden increase in external surface area.

Careful measurements of the characteristic length of the slab-shaped crystals activated at 90°C and 120°C for Sr^{2+} -UPRM-5 (TPA) and Sr^{2+} -UPRM-5 (TBA), respectively, and the length of the same crystals at an activation of 300 °C exhibited a reduction of the average crystal size by up to 44% for the samples prepared with TPA and 35% for the ones prepared with TBA.

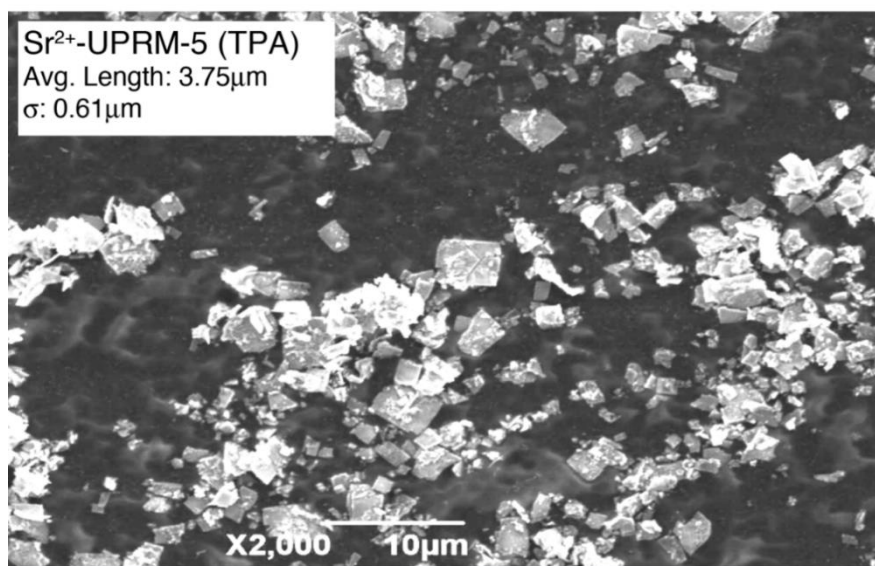


Figure 2.9 SEM micrographs of Sr^{2+} -UPRM-5 (TPA) samples treated at 300°C.

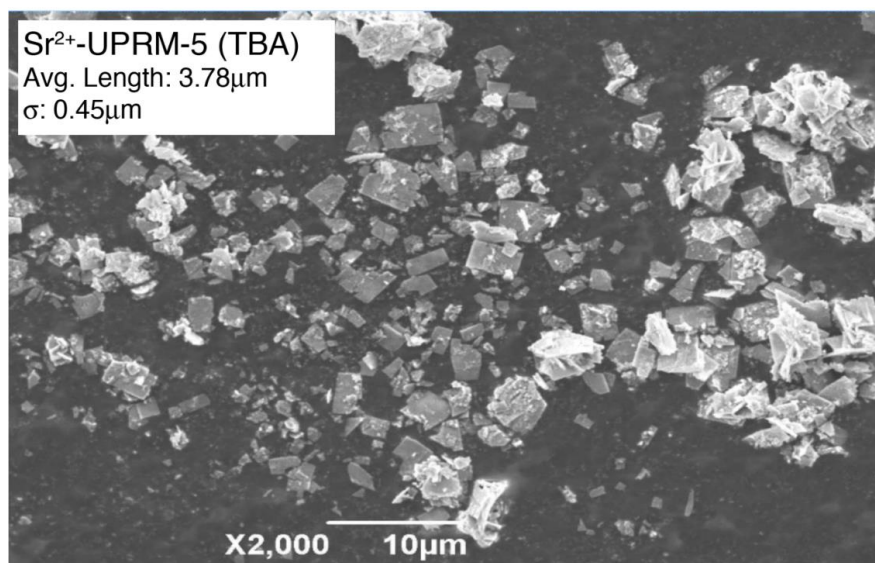


Figure 2.10 SEM micrographs of Sr^{2+} -UPRM-5 (TBA) samples treated at 300°C.

It is important to note that the maximum micropore surface area observed for Sr²⁺-UPRM-5 (TPA), 172 m² g⁻¹, was obtained at a temperature at 90°C, while for Sr²⁺-UPRM-5 (TBA) the maximum (206 m² g⁻¹) was observed at 120°C. These temperatures may correspond to the point for which the mobile water, the water that resides inside the pores, is completely released and to the start of the release of the structural water. As stated previously, for flexible titanosilicates such as ETS-4, the structural or tenacious water appears to be coordinated to the OH groups of the apical oxygen in the semi-octahedral Ti.^{18, 19, 27} The release of such water induces the movement of the semi-octahedral units and this should result in structure contraction.^{28, 29}

2.4.5 Pure Component Carbon Dioxide Adsorption

Analyses done for pure carbon dioxide adsorption at 25°C onto Sr²⁺ exchanged UPRM-5 variants activated or degassed at different temperatures (see Figure 2.11) indicated a trend similar to the one observed for the surface areas (i.e., nitrogen adsorption). This was expected since carbon dioxide molecules have a kinetic diameter that is only slightly smaller than that of nitrogen (i.e., 3.30 vs. 3.65 Å). Maximum carbon dioxide adsorption capacities recorded at 7 atm were ca. 2.80 mmol g⁻¹ (or 11 wt.%) for Sr²⁺-UPRM-5 (TPA) and Sr²⁺-UPRM-5 (TBA) and this took place after the samples were activated at 90 and 120°C, respectively. At higher activation temperatures, the carbon dioxide adsorption at high pressure decreased considerably, suggesting that the pore volume decreased upon contraction of the framework. At 300°C, however, the adsorption behavior observed in the two UPRM-5 materials is quite different in comparison. In the case of Sr²⁺-UPRM-5 (TPA), the adsorption amount at any given pressure decreased by nearly 65%, most likely a result of a severe structural damage to the pore channels during the thermal treatment. For Sr²⁺-UPRM-5 (TBA) the adsorption capacity was reduced only by 32% and could be attributed to a more ordered structure upon thermal treatment (see Figure 2.6).

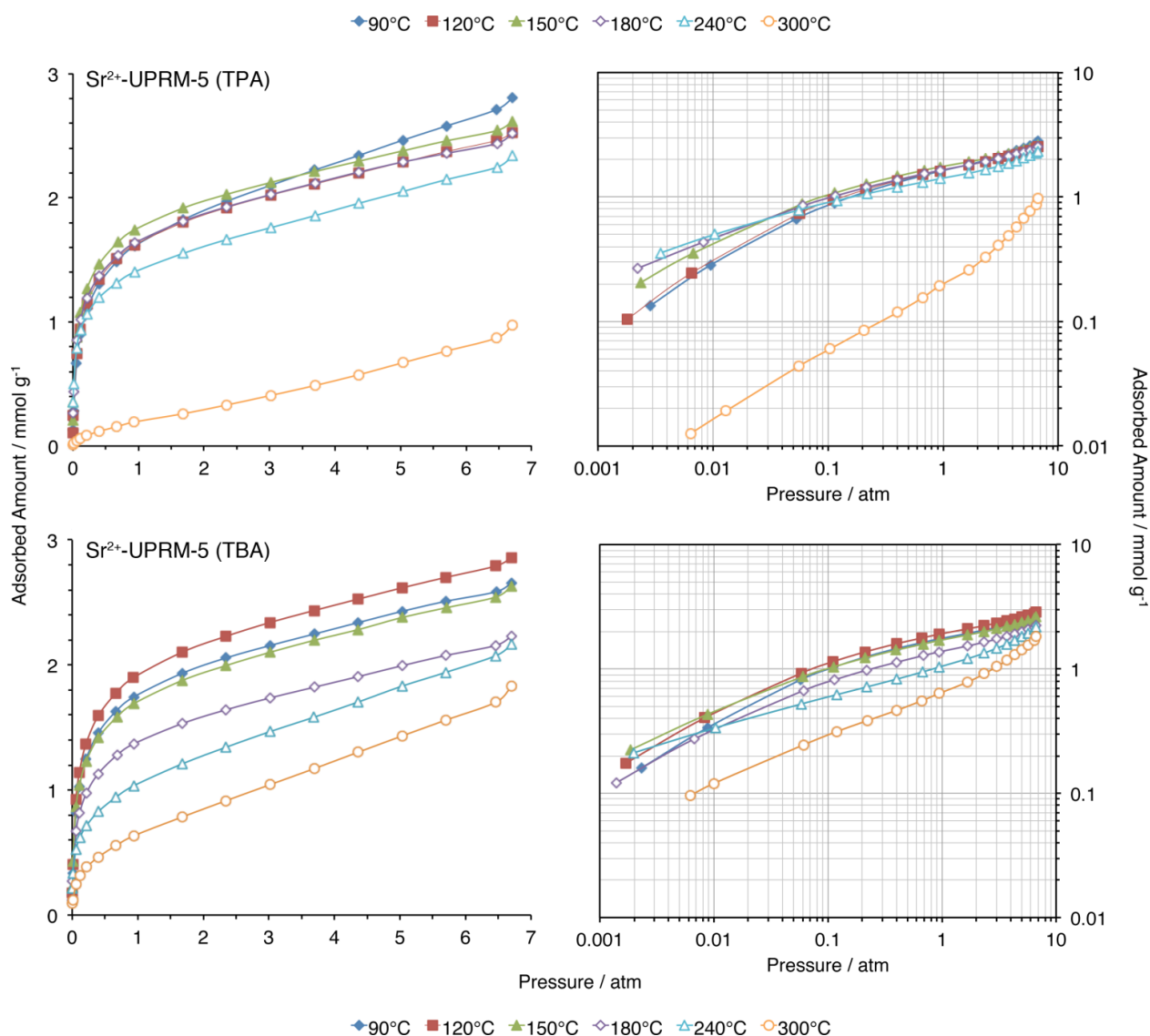


Figure 2.11 Adsorption isotherms for carbon dioxide on for Sr^{2+} -UPRM-5 (TPA) and Sr^{2+} -UPRM-5 (TBA) samples at 25 °C. Adsorbents activated at different temperatures.

A comparison of the CO_2 data gathered for Sr^{2+} -UPRM-5 (TBA) activated at 180 °C with the one gathered Sr^{2+} -UPRM-5 (TEA) variant activated at the same temperature (data reported elsewhere 8) clearly showcases the improvements made to the UPRM-5 structure by employing a larger SDA. For instance, at 0.1 atm, the TBA variant adsorbed about 0.82 mmol/g whereas the TEA variant adsorbed only 0.4 mmol/g at the same pressure. This corresponds to a 50% increase in CO_2 uptake. Since the UPRM-5 variant prepared with TEA collapses after 180 °C, the results clearly suggest

that the variants synthesized with TBA and TPA had a higher thermal stability than the ones previously reported. Higher thermal stability has been attributed in the case of ETS-4 and ETS-10 to a larger amount of octahedral titanium centers⁵, which matches well with the observations made here.

At low pressure, the observed carbon dioxide adsorption amounts followed patterns that reflect the level of interaction between the adsorbate and the adsorbent surface. At higher temperatures, the Sr²⁺-UPRM-5 (TPA) structural contraction process apparently results in a pore systematic collapsing process. The uptake amounts observed in the low-pressure region (< 0.01 atm) increased when the adsorbent activation or degassing temperature was increased up to ca. 240°C. This could be due to the result of overlapping of the interaction potential of the adjacent pore walls, a phenomenon that has been well documented in the literature.³⁰ Since the strontium cations are most likely the preferred carbon dioxide adsorption sites¹ and these would not undergo any hydrolysis³¹, it is possible to assume that water elimination (strongly bound) did not play any role in the low pressure adsorption process. For the case of the Sr²⁺-UPRM-5 (TBA) variant, it appears that its higher thermal stability diminished any surface overlapping effect since the carbon uptake loadings differed considerably only at high pressure (see Figure 2.11). These results suggest that Sr²⁺-UPRM-5 (TPA) materials could be tailored for purification applications (i.e., deep removal of carbon dioxide) whereas Sr²⁺-UPRM-5 (TBA) materials could be tailored for bulk-level separation applications.

2.4.6 Isosteric Heats of Adsorption and Apparent Adsorption Mechanism

Heats of adsorption were estimated for carbon dioxide uptake onto Sr²⁺-UPRM-5 (TPA) and Sr²⁺-UPRM-5 (TBA) materials activated at 90 and 120°C, respectively. The resulting profiles are shown in Figure 2.12. Both UPRM-5 variants showed sorbent-sorbate interactions in the

physisorption range with maxima of 37 and 43 kJ mol⁻¹ for Sr²⁺-UPRM-5 (TPA) and Sr²⁺-UPRM-5 (TBA), respectively. In addition, the isosteric heat profiles resemble those typical of heterogeneous surfaces, which correlated well with the surface heterogeneity parameters obtained after fitting the L-F and D-A isotherms models (see Table 2.2). For the L-F model, a n_{L-F} value greater than 1 translates to a surface that is not homogeneous or Langmuirian. In the case of the D-A model, a n_{D-A} value smaller than 3 is associated to an heterogeneous surface.⁸ However, it is important to keep in mind that among models tested here, only the D-A one takes into consideration the interaction between the adsorbate volume (instead of a monolayer) and the adsorbent surface. This is the typical scenario found in microporous materials. Furthermore, the D-A model parameter C data obtained for each adsorbent variant (see Table 2.2) matched well with the overall trend observed in Figure 2.11. That is, a slightly stronger average interaction between carbon dioxide and the Sr²⁺-UPRM-5 (TBA) materials when compared to that of the other adsorbent variant.

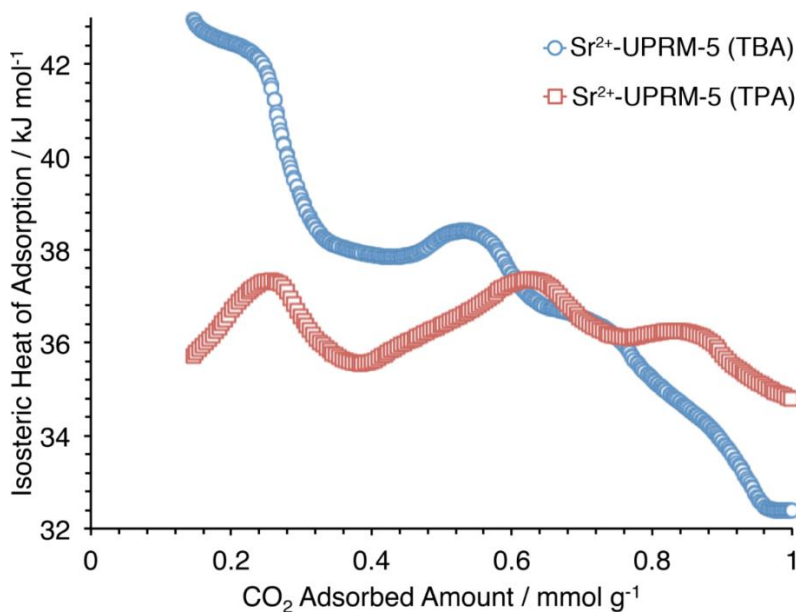


Figure 2.12 Isosteric heats of adsorption of carbon dioxide on for Sr²⁺-UPRM-5 (TPA) and Sr²⁺-UPRM-5 (TBA). Adsorbents activated at 90 and 120 °C, respectively.

Table 2.2 Isotherm models parameters for CO₂ adsorption on strontium exchanged UPRM-5 materials.

Sorbent	Adsorption Temperature (°C)	Langmuir-Freundlich				Dubinin-Astakhov			
		q_o $\left(\frac{mmol}{g}\right)^\S$	n_{LF} (-)	b (atm ⁻¹)	Std. Dev.*	q_o $\left(\frac{mmol}{g}\right)^\S$	n_{DA} (-)	C (-)	Std. Dev.*
Sr ²⁺ -UPRM-5 (TPA) at an activation temp. of 90°C	0	2.90	2.08	7.69	±0.012	2.62	2.24	0.142	±0.010
	25		1.94	1.70	±0.011		2.05	0.166	±0.007
	50		1.95	0.47	±0.006		1.71	0.200	±0.006
	75		1.68	0.29	±0.002		1.73	0.227	±0.001
Sr ²⁺ -UPRM-5 (TBA) at an activation temp. of 120°C	0	2.50	1.92	10.75	±0.012	2.33	2.41	0.139	±0.008
	25		1.70	6.87	±0.009		2.74	0.138	±0.012
	50		1.66	1.47	±0.005		2.25	0.170	±0.007
	75		1.66	0.28	±0.002		1.69	0.230	±0.001

[§] The saturation loadings were estimated at 0°C and assumed constant for the rest of the calculations.

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

The differences seen in the profiles shown in Figure 2.12 were probably due to unique cation positions within the structure and/or different cation loadings. In order to elucidate this, however, it was important to estimate the unit cell composition for each variant. A full elemental analysis was achieved by means of ICP, TGA and MAS-NMR data. The NMR data was employed to fix the relative amount of octahedrally and semi-octahedrally coordinated titanium during the elemental analysis calculations (i.e., amount of OH groups). According to the unit cell composition for Sr²⁺-UPRM-5 (TPA) and Sr²⁺-UPRM-5 (TBA) (see Table 2.3), there is nearly one additional Sr²⁺ cation per unit cell of the former material compared to that of the latter. This could be attributed to significant differences in local coordination environments between the two materials. In addition, both unit cells contain sodium cations that were probably located in sites forbidden to strontium for exchanged. Interestingly, the Si/Ti ratio in both unit cells is nearly identical, but smaller in comparison to what has been reported previously for UPRM-5 and ETS-4.^{1, 32, 33} The Si/Ti ratio obtained for these new UPRM-5 variants could be probably related to less structural

faulting. Given the unit cell data (see Table 2.3), it is evident that the average adsorbate-adsorbent interaction potential (i.e., Figure 2.12) is due to accessibility of carbon dioxide to Sr^{2+} cations rather than the amount of these. Furthermore, since sodium cations relocate themselves across zeolitic frameworks upon dehydration³⁴, some of these may now be located in positions accessible to carbon dioxide. Interaction between the adsorbate and the cation depends on the nature of the latter, among other things, and this should result in an overall heterogeneous surface potential. Hernandez-Maldonado and co-workers³⁵ have shown that for the adsorption of carbon dioxide onto microporous silicoaluminophosphate materials, the adsorbate undergoes stronger interactions with strontium as compared to sodium cations. Assuming that the same applies to the UPRM-5 adsorbents, the adsorbed amounts of carbon dioxide corresponding to the first inflection points observed in the isosteric heat of adsorption profiles (see Figure 2.11) should correspond to occupancy of all of the available strontium sites. Using unit cell data corrected for the amount tenacious water remaining after degassing, the aforementioned heat of adsorption profile heat of adsorption profile inflection points should translate to about 0.46 and 0.37 carbon dioxide molecules per unit cell for Sr^{2+} -UPRM-5 (TPA) and Sr^{2+} -UPRM-5 (TBA), respectively. Since the observed adsorption energy is larger in the latter adsorbent, it is plausible to state that the Sr^{2+} environment in that sample is more favorable for interaction with carbon dioxide. This could be attributed to the level of faulting and the corresponding locations, in which cations have to position themselves in order to compensate for all of the charge deficiencies in the titanium silicate framework.

Table 2.3 Unit cell composition of strontium exchanged UPRM-5 materials.

Sample	Unit Cell
Sr^{2+} -UPRM-5 (TPA)	$ \text{Sr}_{3.0}^{2+}\text{Na}_{3.3}^{+}\text{OH}_{2.3}^{-} [\text{Si}_{11.4}\text{Ti}_{8.3}\text{O}_{37}]:23\text{H}_2\text{O}$
Sr^{2+} -UPRM-5 (TBA)	$ \text{Sr}_{2.4}^{2+}\text{Na}_{3.9}^{+}\text{OH}_{1.5}^{-} [\text{Si}_{9.3}\text{Ti}_{7.1}\text{O}_{37}]:20\text{H}_2\text{O}$

2.4.7 Pure Component Adsorption Isotherms for Carbon Dioxide, Methane and Nitrogen

Adsorption data at 25 °C for different gases in the strontium-based adsorbents were gathered after employing optimal activation or degassing temperatures (i.e., those resulting in overall larger carbon dioxide loadings). These were 90 and 120 °C for Sr^{2+} -UPRM-5 (TPA) and Sr^{2+} -UPRM-5 (TBA), respectively. According to the results shown in Figure 2.13 both adsorbents displayed remarkable selectivity towards carbon dioxide. This is mainly due to an enhanced interaction between the large carbon dioxide quadrupole moment and the electric field generated by the extra-framework divalent cations. Since the quadrupole moment of carbon dioxide is about three times larger than that of nitrogen and methane does not have any quadrupole moment (see Table 1.1), this will result in an enhanced surface electrostatic potential.^{36, 37} However, both adsorbent materials also displayed better selectivity toward methane over nitrogen. This could be attributed to the methane octopole moment that appears when it is in contact with the cation electric field.^{36,}

38-40

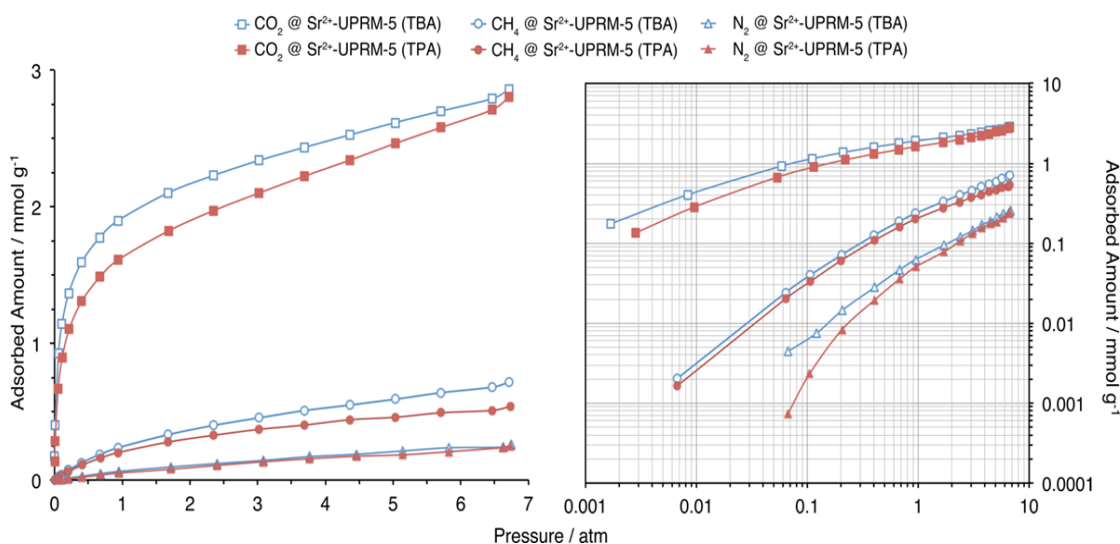


Figure 2.13 Pure component adsorption isotherms for carbon dioxide, methane and nitrogen on Sr^{2+} -UPRM-5 (TPA) and Sr^{2+} -UPRM-5 (TBA) at 25 °C. Adsorbents activated at 90 and 120 °C, respectively.

Figure 2.13 also shows greater uptake of carbon dioxide in the Sr^{2+} -UPRM-5 (TBA) adsorbent when compared to the other variant. This is directly related to the data shown in Figure 2.12 and should be a result of favorable surface and textural properties brought by the use of TBA as an SDA during the synthesis of UPRM-5.

Finally, both of the UPRM-5 variants presented in this work exhibited superior adsorption capacities when compared to other porous titanasilicates. At atmospheric conditions, Sr^{2+} -UPRM-5 (TBA) materials adsorbed at least 40% more CO_2 when compared to barium or copper exchanged ETS-4.⁴¹ A similar result was found when compared to materials that are analog to ETS-4, namely the RPZ (reduced pore size) titanium silicate series. Both UPRM-5 variants also showcased larger single point selectivity values (CO_2/CH_4 @ 1 atm) when compared to the aforementioned titanasilicate materials, with the exception of Ba^{2+} -RPZ. However, the maximum CO_2 swing capacity for the later was ca. 0.4 mmol per gram of adsorbent⁴¹, which is at least three times smaller when compared to the capacities exhibited by both Sr^{2+} -UPRM-5 variants.

2.5 Concluding Remarks

Two new UPRM-5 variants have been obtained by employing microwave assisted heating and TPA or TBA. According to XRD and MAS NMR data, the NR_4^+ species apparently act as SDAs during the synthesis of the porous frameworks. In particular, each quaternary ammonium cation produced structures with unique level of faults as evidenced by the titanium coordination environments. Furthermore, upon detemplation and ion exchange with Sr^{2+} each UPRM-5 variant displayed higher thermal stability ranges when compared to other titanium silicates. This was verified via *in situ* high temperature XRD and surface area measurements at temperatures up to and greater than 300°C. In summary, UPRM-5 can be modified considerably at a structural and textural level by the use of larger alkyl ammonium based SDAs. This controls and enhances its

thermal stability and ensures a superior selectivity toward carbon dioxide. The former is critical for applications that rely on thermal swing operations, where framework stability is imperative. It also shows the potential of modified titanium silicates as a feasible and economical option for several applications such as natural gas purification. More specifically, the results suggest that Sr^{2+} -UPRM-5 (TPA) materials could be tailored for applications in which deep removal of carbon dioxide is needed whereas Sr^{2+} -UPRM-5 (TBA) materials could be tailored for bulk-level separation applications.

2.6 References

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Chapter 3

Long- and Local-Range Structural Changes in Flexible Titanium Silicates with Variable Faulting Upon Thermal Treatment and Corresponding Adsorption and Particle Size Polydispersity-Corrected Diffusion Parameters for CO₂/CH₄ Separation

3.1 Chapter Summary

In this chapter, we studied thermally induced structural changes in Sr²⁺-UPRM-5 variants prepared using tetrapropylammonium (TPA) and tetrabutylammonium (TBA) and their correlation to the diffusion of CO₂ and CH₄ at 25°C. Both Sr²⁺-UPRM-5 materials contained different amounts of structural faulting that are correlated to the formation of 12-14 MR pores. *In situ* high-temperature X-ray diffraction revealed structural changes corresponding to orthorhombic phases up to 300°C. Analysis of *in situ* high-temperature ²⁹Si magic angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy revealed new silicon environments surrounding the archetypical Si(2Si, 2Ti_{oct}) and Si(3Si, 1Ti_{semi}oct) coordination centers. MAS NMR data analysis indicated that the Si environment in Sr²⁺-UPRM-5 (TPA) appears to be more susceptible to changes upon thermal treatment. A phenomenological volumetric transport model corrected for particle size polydispersity was used to estimate diffusion constants at 25°C in adsorbents preactivated at different temperatures. At the optimal conditions, the CO₂/CH₄ kinetic selectivities were 41 and 30 for Sr²⁺-UPRM-5 (TBA) and (TPA), respectively.

3.2 Introduction

Consumption of natural gas is now ramping up at an incredible pace due to shale gas fracturing expansion and the development of newer fracking technologies, allowing access to supplies that were unavailable before.¹ Therefore, methods to increase the efficient consumption of natural gas

are mandatory to moderate its CO₂ emissions. Furthermore, the presence of CO₂ in gas mixtures also brings operational problems since it induces severe pipeline corrosion.²⁻⁴ Since CO₂ contains no heating value, its removal is also critical to avoid a considerable decrease in methane's (CH₄) true energy supply potential.^{5, 6}

Many CO₂ capture technologies have been developed and employed during the last two decades, being the process of absorption by aqueous amines the most commonly used. In fact, this is one of the most matured and well established technologies in the natural gas industry. It permits for rapid cycling with a sustained CO₂ removal capacity. Most amines have also good thermal stability and reactivity, and allows for the removal of H₂S along with CO₂. However, these benefits come at the expense of considerable energy requirements due to high regeneration temperatures for which not all of the amine solvent can be re-used. The process also inherently involves the use of highly corrosive solvents and their disposal can become an environmental hazard.^{5, 7} More recently, separation by hydrates and membranes has been proposed for CO₂ removal from CH₄ effluents.^{6, 8-10} These have emerged during the last couple of years as sound methods due to low cost, fewer energy requirements, simple process flow schemes, and ease of operation.¹¹⁻¹³ However, there are some drawbacks in the use of some of these technologies such as low chemical/thermal stability and inefficiency in reducing CO₂ concentrations upon long term operation.¹³

Another proposed alternative as competitive CO₂ remediation technology is the use of adsorbents in pressure swing adsorption (PSA) processes at ambient temperature.¹⁴⁻¹⁶ Among many of the adsorbents that have been tested for PSA in the past, metal-based adsorbents, activated carbon and zeolites have seen the greatest degree of commercial success.¹⁶⁻¹⁸ This is mainly due to an overall reduction in energy use by the process. In addition, the relatively weak interactions between the adsorbate and the adsorbent result in ease of regeneration of the latter, requiring lower mechanical

energy input that the equivalent needed for regeneration of amine solvents. In addition, the incorporation of these types of adsorbents in PSA systems could result in less capital and maintenance costs.¹⁰ Most recently, certain metal organic frameworks (MOFs) have been also identified as highly selective toward CO₂^{4, 19-22} and, therefore, offer tremendous potential for PSA. Different from other adsorbents in which thermodynamic equilibrium dominates the adsorption process, some of the most recent MOFs perform CO₂/CH₄ separations based on differences in the rate of adsorption.^{19, 20} However, for kinetic separations to effectively take place during PSA operations, the size of the pores must be fairly closed to that of the gas molecules to be adsorbed.²⁰ For most MOFs, the pore size specifications needed for CO₂/CH₄ kinetic separation cannot be obtained by means of simple post-modification procedures. However, certain zeolitic formulations with pore sizes in the 3-4 Å range have been reconsidered for kinetic separations. Their relative ease of preparation and working capacities are attractive characteristics for the removal of CO₂ from flue gas, but their potential to increase their selectivity toward CO₂ remains limited.⁵

Flexible titanium silicates represent a good alternative to develop CO₂ selective adsorbent platforms due to their capacity for pore size reduction upon thermal dehydration and ease of modification for increasing its selectivity towards CO₂. ETS-4 was the first of these materials and it is considered the standard in terms of adsorbents for the separation of similar size molecules such as CO₂, N₂ and CH₄.^{5, 23-30} However, upon thermal activation the material working adsorption maximum capacity is considerably reduced as consequence of the structural contraction, which translates to more adsorption/regeneration cycles.³¹ In this regard, UPRM-5, has exhibited larger surface area in comparison with ETS-4, as well as larger adsorption capacities toward CO₂. It was found that the UPRM-5 textural properties as well as thermal stability can be modified and controlled depending on the level of faulting in the structure, which can be adjusted depending on

the type of quaternary ammonium cation employed as structure directing agent (SDA).³² For instance, as shown in Chapter 2, the use of tetrapropylammonium (TPA) and tetrabutylammonium (TBA) improved the UPRM-5 structural and textural characteristics for the adsorption of CO₂ in a considerable fashion.³² A recent study by Yu et al. also showed the potential of using Sr²⁺-UPRM-5 prepared with tetraethylammonium (TEA) for the selective N₂ removal in natural gas upgrading.³³ The contraction property of UPRM-5 upon thermal treatment was used to reverse selectivity in favor of N₂, as has been done before for ETS-4.^{25, 34}

Superior selectivity in Sr²⁺-UPRM-5 toward CO₂ suggests that CO₂/CH₄ kinetic separation can also be possible. Furthermore, the two UPRM-5 variants that had showcased the best performance for CO₂ removal so far have been Sr²⁺-UPRM-5 (TPA) and Sr²⁺-UPRM-5 (TBA).³² Therefore, the present chapter focuses in the determination of the potential role of UPRM-5 prepared with different degrees of faulting to separate CO₂/CH₄ based on both equilibrium and kinetic differences. The latter was based on diffusion data gathered using a volumetric transport model corrected for adsorbent particle size polydispersity. In addition, we have studied long and local range structural changes produced upon thermal contraction via indexing of *in situ* high temperature X-ray diffraction (XRD) and ²⁹Si magic angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy, respectively. The thermal contraction characteristics were correlated to the adsorbents performance for CO₂/CH₄ separation at different activation temperatures in attempt to understand the connection between faulting and performance and, therefore, pave the way to develop superior adsorbents based on the same platform.

3.3 Experimental Procedure

3.3.1 UPRM-5 Synthesis and Functionalization

The UPRM-5 variants considered for this work were synthesized by microwave-assisted hydrothermal reactions following methods available elsewhere.^{31, 32} Reaction times were 12 and 20 hrs when employing tetrapropylammonium (TPA) and tetrabutylammonium (TBA) as SDAs, respectively. Detemplation and further modification of the samples were made by liquid ion-exchange with NH_4^+ and Sr^{2+} also using methods reported elsewhere.^{32, 35} For ease of identification the strontium modified materials will be labeled Sr^{2+} -UPRM-5 (TPA) and Sr^{2+} -UPRM-5 (TBA) depending on whether tetrapropylammonium or tetrabutylammonium cation were employed as SDAs.

3.3.2 Material Characterization

Scanning electron microscopy (SEM) images were captured using a JEOL-JSM-6930LV unit working at a voltage range of 5.0–20.0 kV. The images were obtained following standard procedures for low conductive samples. The micrographs were used to determine the material morphology and particle length (x) distribution via direct sampling. The length distribution was then fitted to a cumulative gamma (Γ) distribution function, $P(x)$:

$$P(x, \alpha, \beta) = 1 - \frac{1}{\beta^\alpha \Gamma(\alpha)} x^{\alpha-1} e^{-\frac{x}{\beta}} \quad (3.1)$$

where α and β are the shape parameters of the distribution.

In situ high-temperature XRD data were collected using a high temperature Reactor X (Rigaku Corporation) module attached to a Rigaku Ultima III system. This system allows enclosure of the sample powder with different gas atmospheres while permitting passage of X-rays through a

continuous beryllium window and heating of the sample through an infrared-based heating element. The samples were placed onto a removable black quartz plate and the temperature measured using a 1/16" diameter thermocouple that was placed inside an equally sized cylindrical hole located on one side of the quartz plate for accurate measurements. X-ray scans were gathered at $3.5^{\circ} \text{ min}^{-1}$ while the sample was heated from room temperature to 300°C at $1^{\circ} \text{C min}^{-1}$ by flowing in helium (Ultrahigh Purity Grade, Praxair) at 60 mL min^{-1} . The resulting XRD data were indexed using the CRYSFIRE and the TREOR-90 routines.^{36, 37}

In situ high temperature ^{29}Si MAS NMR spectra were collected on a Bruker DRX300NMR spectrometer with the ^{29}Si Larmor frequency of 59.63 MHz and using a 4 mm Bruker double-resonance variable temperature MAS probe. A $3.0 \mu\text{s}$ pulse ($\sim 30^{\circ}$ flip angle) was used for excitation of the ^{29}Si magnetization. A total of 8192 scans were used to accumulate the signals with a recycle delay of 5 s, except for the experiments during the cooling path at 135 and 72°C in which 4096 scans were used. The samples were sealed into NMR rotor and spun at 6 kHz using N_2 gas. The temperature was controlled within $\pm 0.1^{\circ}\text{C}$ by a Bruker BVT-2000 unit. The temperature was ramped from a temperature to the next higher temperature at a rate of $10^{\circ}\text{C min}^{-1}$ and then stabilized for about half an hour before data acquisition. The temperature was carefully calibrated independently using a lead nitrate sample spinning at 6 kHz by monitoring the plot of the ^{207}Pb chemical shift versus temperature. The chemical shift was referenced to DSS at 0 ppm. 40 Hz exponential line broadening was used in the spectra. All spectra were deconvoluted using the SpinWorks NMR software.

3.3.3 Adsorption Equilibrium Isotherms and Fractional Uptake Data.

Single-component CO_2 and CH_4 adsorption equilibrium data were gathered volumetrically using a Micromeritics ASAP 2050 unit. The isotherms were obtained at 25°C and pressures up to 7 atm.

Degas or activation of the samples were carried out at 90 and 180°C for Sr²⁺-UPRM-5 (TPA) and, 120 and 180°C for Sr²⁺-UPRM-5 (TBA), both under vacuum for 18 h. The first temperature corresponds to the optimal condition to achieve the largest surface area (i.e. 217 and 261 m² g⁻¹, for Sr²⁺-UPRM-5 (TPA) and Sr²⁺-UPRM-5 (TBA) respectively) while the second one yields a reduction of surface area of 65 – 84% depending on the adsorbent variant.³² Ultra-high purity (Praxair) grade CO₂ and CH₄ were used as received. The adsorption equilibration time was set to at least 100 seconds and the apparent equilibrium state corroborated by a near-zero slope condition present in at least eleven consequent pressure transient points (i.e., a total of 1100 seconds worth of data per section per pressure step).

Fractional uptake data were gathered volumetrically using a Micromeritics ASAP 2020 instrument fitted with a turbo molecular drag pump. The data were collected at steps of 0.1 s and different pressures. In addition, the uptake data were corrected to compensate for the ASAP 2020 equipment effective dead time (ca. 0.3 s) and for any instability caused by the system.³⁸ The suitability of using a volumetric phenomenological transport model was carefully evaluated to determine the diffusional behavior of the studied gases into the adsorbents.

3.4 Results and Discussion

3.4.1 Long Range Thermally Induced Framework/Pore Contraction

Thermally induced long range structural changes in either Sr²⁺-UPRM-5 (TPA) or Sr²⁺-UPRM-5 (TBA) were analyzed via *in situ* high temperature XRD. A set of diffraction patterns gathered from 30 to 300°C is shown in Figure 3.1. Unit cell parameters for both Sr²⁺-UPRM-5 variants are shown in Table D.1 and corresponded to an orthorhombic symmetry, which correlates well with the results recently reported for the crystal refinement of Na⁺-UPRM-5 prepared with TEA.³⁹ The structure and faulting in this variant were described via stacking of orthorhombic and triclinic

polymorph phases, but the former is the predominant one (90%). The Sr^{2+} -UPRM-5 (TBA) lattice parameters shown in Table D.1 are also similar to the ones reported for Zorite, the natural counterpart of ETS-4.⁴⁰⁻⁴³ In the case of Sr^{2+} -UPRM-5 (TPA) activated at 90°C, lattice parameters b and c appeared to be larger in comparison to those of Sr^{2+} -UPRM-5 (TBA), but upon dehydration also become similar to those of Zorite.

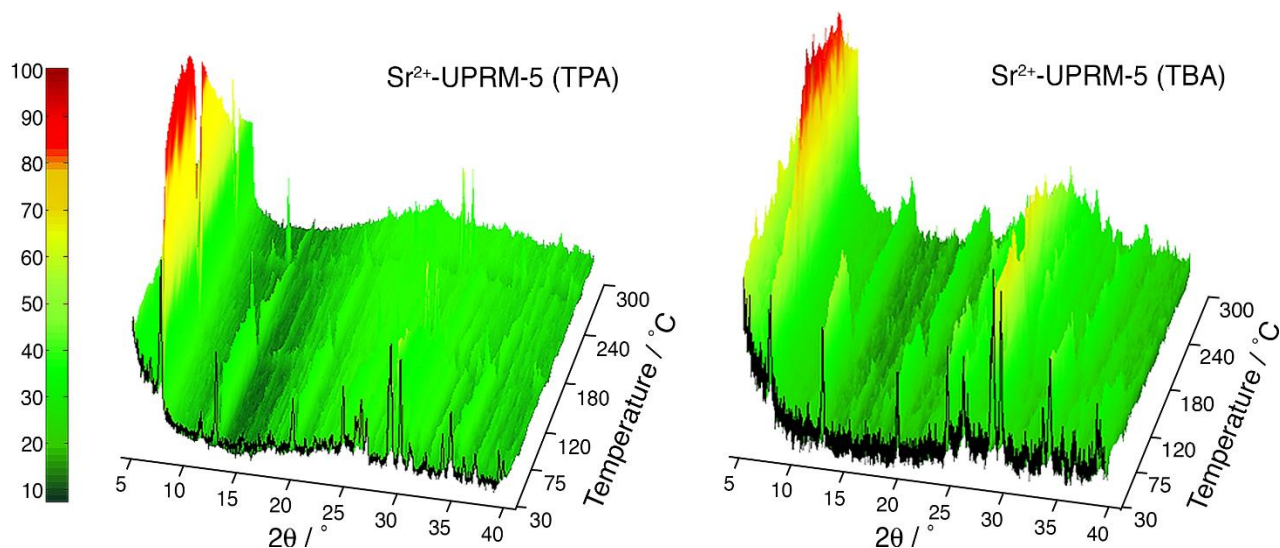


Figure 3.1 *In situ high temperature XRD profiles for Sr^{2+} -UPRM-5 prepared with different SDAs.*

Framework contraction upon thermal treatment occurred uniformly as evidenced by the unit cell dimensions for both materials (see Table D.1). Sr^{2+} -UPRM-5 (TPA) showed a total unit cell volume reduction of ca. 32% when treated from 90 to 300 °C. The overall reduction involves a dual step contraction process, namely 90 → 180°C (step I) and 240 → 300°C (step II), probably related to the two step dehydration mechanism previously reported based on thermal gravimetric analyses.³² Sr^{2+} -UPRM-5 (TBA), on the other hand, exhibited a single step unit cell volume reduction of ca. 7% in the 90 → 300 °C range. Lattices b and c exhibited the largest reduction at high temperatures, especially for Sr^{2+} -UPRM-5 (TPA). Lattice parameter c is plausibly associated to the 8-member ring (8-MR) channels or pores.³⁹ It is also believed that these pores should

dominate gas adsorption kinetics since they can be size tailored in Sr^{2+} -ETS-4 to separate similar size gas molecules.⁴⁴ The reduction in c dimensions within the 90 $\rightarrow$ 180 °C range was of 14 and 4% for Sr^{2+} -UPRM-5 (TPA) and Sr^{2+} -UPRM-5 (TBA), respectively. Therefore, it should be expected that if these 8-MR pores restrict access to the UPRM-5 framework, Sr^{2+} -UPRM-5 (TPA) should showcased the best molecular gate effect.

3.4.2 *In situ* ^{29}Si MAS NMR

The MAS NMR tests were performed to elucidate the local range structural changes related to the different titanium coordination states that could arise upon an increase in activation temperature and attempt to correlate this to the choice of SDA employed during the synthesis of UPRM-5. Figure 3.2 shows the experimental *in situ* ^{29}Si MAS NMR and deconvoluted spectra for both Sr^{2+} -UPRM-5 (TPA) and (TBA) variants, as well as the difference spectrum between the experimental spectra and the total deconvolution. Two silicon environments were initially found in both UPRM-5 variants, similar to what has been reported for other titanium silicates. One is related to the octahedral titanium centers, $\text{Si}(2\text{Si}, 2\text{Ti}_{\text{oct}})$, located at around -93.0 ppm, while the other one is related to the semi-octahedral titanium centers, $\text{Si}(3\text{Si}, 1 \text{Ti}_{\text{semi-oct}})$, located at around -97.0 ppm.^{29, 31, 32, 45} When increasing the temperature from 60 to 150°C, the spectral stack shows a third resonance centered originally at around -89.0 ppm, which is also related to the $\text{Si}(2\text{Si}, 2\text{Ti}_{\text{oct}})$ environment. This is more apparent in Figure 3.3, which shows chemical shifts and peak relative areas as a function of temperature. Chemical shifts for both materials remained similar and nearly constant up to temperature of 60°C. However, as the temperature was increased further, peak relative areas underwent significant changes. As the temperature is increased, the relative area of the resonance associated to the semi-octahedral titanium centers decreases. Semi-octahedral titanium chains (or larger amount of structural faulting) are also associated to tenacious or

coordinated water present in flexible titanium silicates.^{23, 46} Sr^{2+} -UPRM-5 (TPA) exhibited the most significant reduction in the amount of semi-octahedral titanium centers, from ca. 50% to ca. 28%, within the 30 - 150°C range. Since faulting in these materials will translate to significant differences in textural properties, the NMR data suggests that such properties plausibly correlate with the level of dehydration of the semi-octahedral titanium centers.

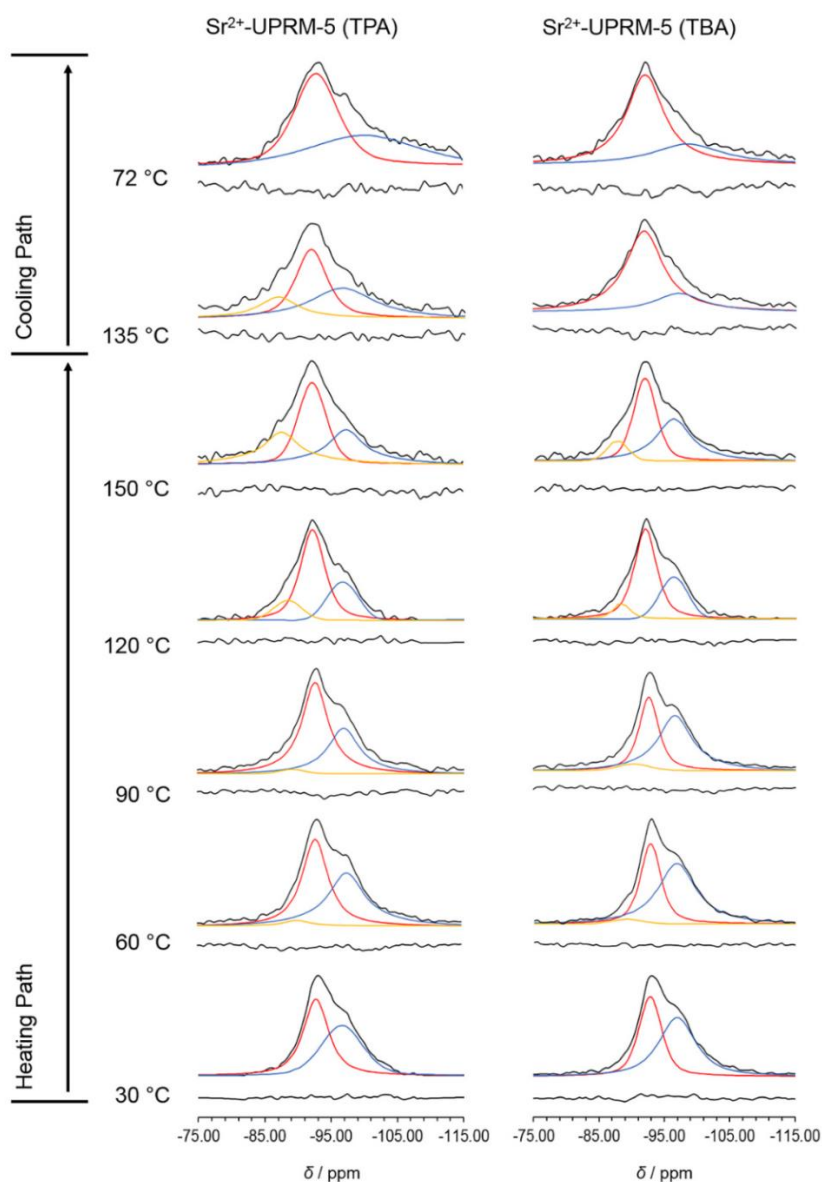


Figure 3.2 In situ high temperature ^{29}Si MAS NMR spectra Sr^{2+} -UPRM-5 prepared with different SDAs. The difference spectrum between the total deconvolution and experimental data is also shown.

Peak relative areas associated to octahedral titanium centers reached a maximum at 90 and 120°C for Sr²⁺-UPRM-5 (TPA) and Sr²⁺-UPRM-5 (TBA), respectively. It is also worth noting that the peak relative area associated to the Si(2Si, 2Ti_{oct}) environment increased when the temperature was increased, markedly in the case of Sr²⁺-UPRM-5 (TPA). The appearance of the corresponding resonance (i.e., initially centered at -89.0 ppm) and further increase in the peak relative area may be the consequence of perturbations of the octahedral titanium centers due to the release of coordinated water. This also seems to affect the semi-octahedral titanium centers.

Material dehydration and plausibly thermal stress appear to also induce re-location of the Sr²⁺ cations, as suggested by the chemical shifts of the resonances related to the Si(2Si, 2Ti_{oct}) environments and initially located at -93.0 ppm and -89 ppm. Such phenomenon may occur due to de-shielding of silicon atoms at temperatures higher than 90°C. In general, these local changes seem related to framework contraction in Sr²⁺-UPRM-5 and, therefore, could dictate adsorption and textural properties for UPRM-5 adsorbents. Such changes have shown to be more significant, however, in the case of Sr²⁺-UPRM-5 (TPA) and indicates perhaps more sensitivity toward thermal stimulus.

An attempt to verify the reversibility of the formation of the new titanium environments was made by lowering the temperature after the heating stage of the *in situ* 29Si MAS NMR experiments (see Figure 3.2). The resonance located at -89 ppm suffered a decrease in intensity and, in the case of Sr²⁺-UPRM-5 (TPA), it was finally absent in the spectrum upon cooling to 72°C. For the Sr²⁺-UPRM-5 (TBA) material, this resonance disappeared upon cooling to 135°C. The level of noise in the samples spectra at 150°C correlate with some level of atomic disorder due to material dehydration. Sr²⁺-UPRM-5 (TPA) seems to exhibit the higher level of disorder. Decreasing the temperature to 135°C increased the signal noise, more so for the case Sr²⁺-UPRM-5 (TPA).

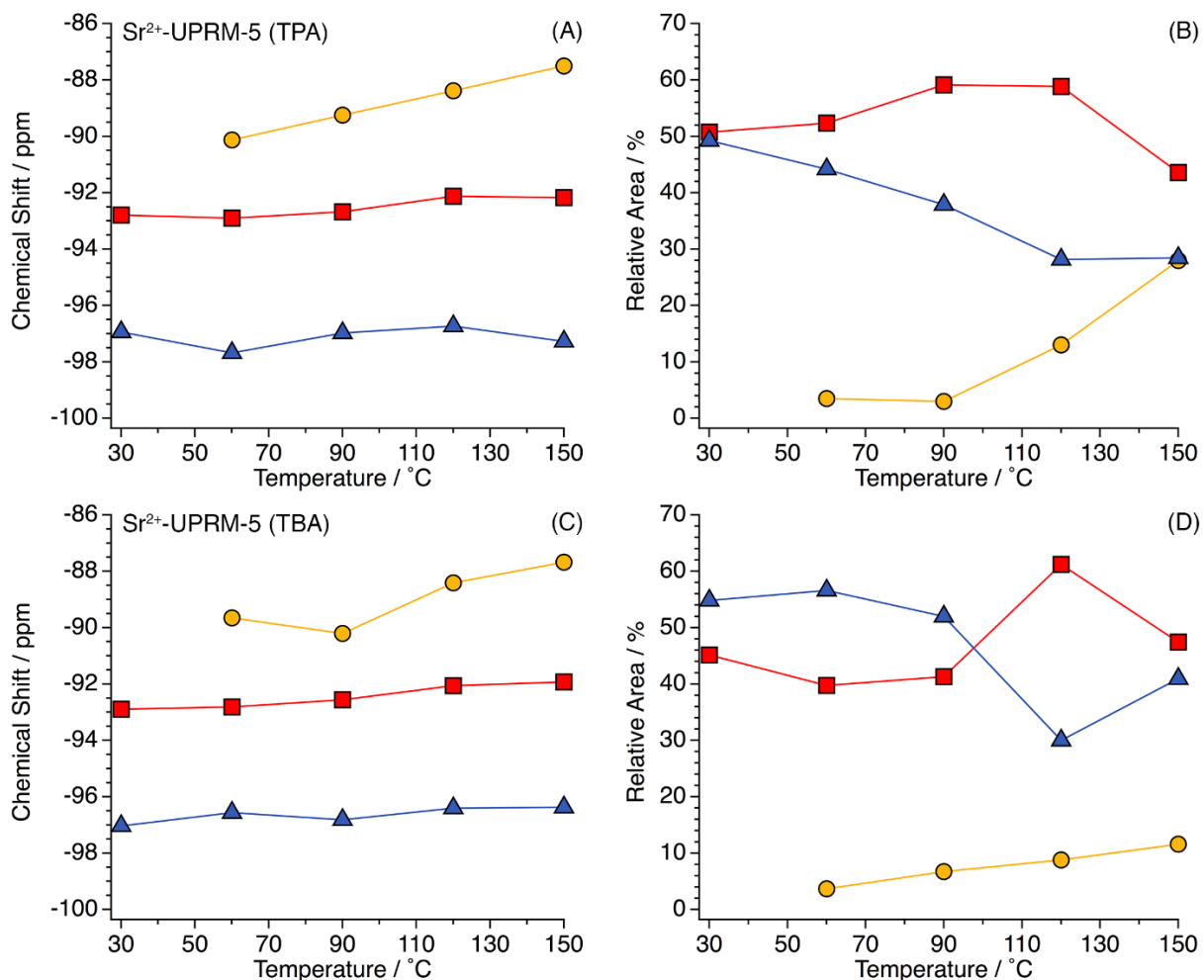


Figure 3.3 ^{29}Si MAS NMR chemical shifts and relative peak area as function of temperature of deconvoluted spectra for (A, B) Sr^{2+} -UPRM-5 (TPA) and (C, D) Sr^{2+} -UPRM-5 (TBA).

Since the NMR sample was sealed inside the rotor, the water that was removed from the framework during the heating phase of *in situ* NMR tests was probably available to re-adsorb onto the sample, but with limited fashion probably due to equilibrium considerations. If this hypothesis holds, then it is evident that the process is more detrimental to Sr^{2+} -UPRM-5 (TPA). It should be noted that a significant broadening of the peak related to the $\text{Si}(3\text{Si}, 1 \text{Ti}_{\text{semi-oct}})$ was observed for both UPRM-5 samples, as well as a reduction in the corresponding relative peak area upon cooling and/or rehydration.

3.4.3 Single Component Equilibrium Adsorption

Figure 3.4 shows pure or single component equilibrium adsorption data gathered for both CO₂ and CH₄ at 25 °C on adsorbent variants that were pre-activated at the optimal temperature (i.e., to achieve maximum accessible surface area) or at 180°C to elucidate effects of structural contraction. Please refer to the experimental section for more information regarding the choice of activation temperatures. Upon activation at 180°C, the adsorbent prepared based on TPA displayed an increase in CO₂ loading at low pressures probably due to overlapping of the surface interaction potential as part of the structural contraction. This enhances the interactions between the neighbor adsorption sites and the adsorbate. A slight increase was observed for CH₄ adsorption as well, but it is minimal in comparison probably due to the absence of a quadrupole moment contribution to the total interaction potential. That is, the interactions are mostly based on the surface electric field with the polarizability of the adsorbate.¹⁵ In the case of the adsorbent variant prepared with TBA, a decrease in CO₂ adsorption upon activation of the adsorbent at 180°C was probably also due to contraction of the structure. This was observed at any gas pressure, which contrasts with the loading profiles observed in Sr²⁺-UPRM-5 (TPA). Inspection of the CH₄ adsorption isotherms show an increase in loading upon activation of the Sr²⁺-UPRM-5 (TBA) adsorbent at 180°C, probably due to, once again, an enhanced adsorbate-adsorbent interaction brought by a surface potential overlapping. However, since this phenomenon appears to be absent during the adsorption of CO₂ onto the Sr²⁺-UPRM-5 (TPA) adsorbent variant, a possible explanation lies on the bimodal pore system displayed by these materials.³⁹

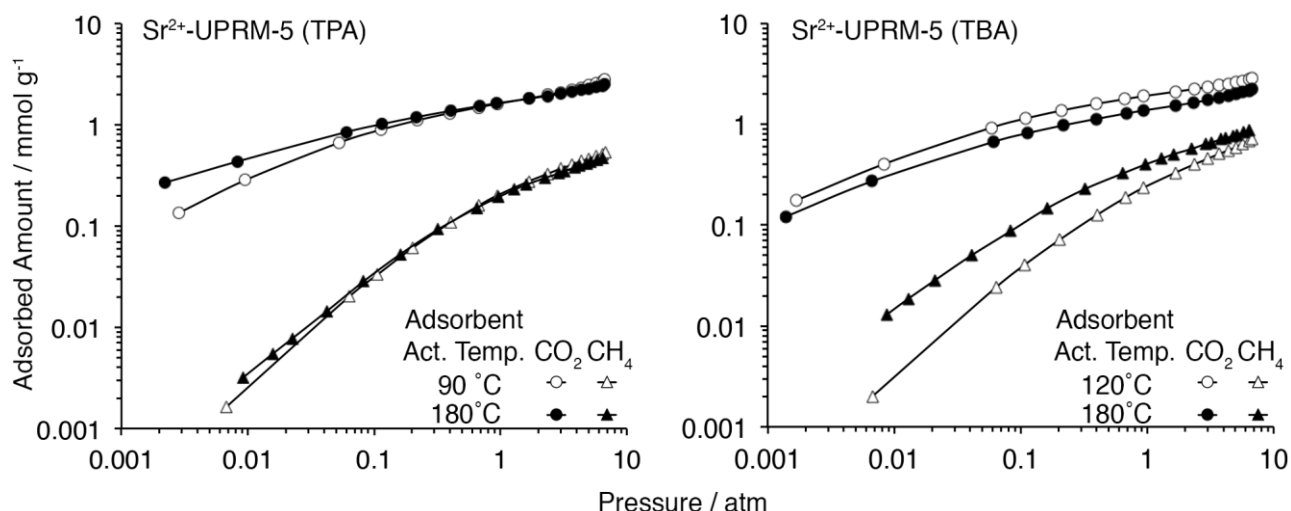


Figure 3.4 Single component CO_2 and CH_4 adsorption equilibrium isotherms gathered at 25°C. The adsorbents were activated at the corresponding optimum activation temperatures (i.e., 90 and 120°C) and at 180°C.

As reported recently for Sr^{2+} -UPRM-5 prepared using TEA, these materials have a set of two accessible pore channels each with different dimensions.³⁹ Adsorption studies made for ETS-4, which also contains a bimodal pore system, have shown that this feature results in poor prediction of adsorption/desorption diffusivities when traditional phenomenological transport models are employed.^{25, 33} The narrower channels in UPRM-5 correspond to the 8-MR pore system previously mentioned, which is characteristic of flexible titanium silicates.^{23, 39, 44} The other dominant pore system is a result of the structural faulting, which is controlled by the choice of SDA and effectively results in larger pore dimensions.³⁹ Per the discussion of the XRD results, the 8-MR pores or channel system in Sr^{2+} -UPRM-5 (TPA) and Sr^{2+} -UPRM-5 (TBA) seems to be the most affected by thermal contraction during thermal activation. Also, due to the similarity in sizes between the 8-MR pore opening and the kinetic diameter of the adsorbates, i.e. CO_2 and CH_4 , these pores can be tailored for effective molecular sieving and, therefore, exert some control on the gas transport through the structure framework.

In the case of Sr^{2+} -UPRM-5 (TPA), which contains the largest amount of structural faulting, it appears that the 8-MR pores are easily accessible only to CO_2 molecules. In fact, it seems that the pore dimensions could be anywhere between 3.3 and 3.8 Å, the kinetic diameters of CO_2 and CH_4 , since there is little difference in CH_4 loading upon an increase in activation temperature. CH_4 is probably adsorbing preferentially onto the surface provided by the second pore system that arises from the structural faulting. Since the data shown in Figure 3.4 do not exhibit saturation plateaus, it is possible to assume that the dimensions of this secondary pore system are large enough to avoid significant loss in void volume upon thermal contraction up to 180°C (relative to the dimensions of the adsorbates). The same cannot be stated in the case of Sr^{2+} -UPRM-5 (TBA). The fact that this variant exhibits less faulting seems to translate to 8-MR pores that have dimensions larger than 3.8 Å, probably due to less twisting or contraction upon thermal treatment. The sudden increase in CH_4 loading upon treatment of the TBA based adsorbent pre-activated at 180°C is probably due to enhanced interactions with an overlapping surface upon pore contraction. Upon an increase in CH_4 pressure, the loading approaches that of the adsorbent treated at 120°C, suggesting yet again that the pore dimensions are closer to those of CH_4 . However, this contraction does not bring any enhanced interactions with CO_2 probably due to the smaller dimensions of this adsorbate. Similar trends should be observed during rates of adsorption and this will be discussed next.

3.4.4 Gas Fractional Uptakes and Diffusion Time Constants

CO_2 and CH_4 fractional uptake data were gathered for both Sr^{2+} -UPRM-5 (TPA) and Sr^{2+} -UPRM-5 (TBA) at 25°C and different adsorbent activation temperatures. Figure 3.5 shows uptake profiles gathered at a gas pressure of ca. 0.005 atm, which was close to the lowest pressure range monitored during the experiments and represents a condition for slow diffusion measurements (i.e., limiting kinetics). A quick inspection of the data shows what appear to be similar uptake rates for CH_4

adsorption onto Sr^{2+} -UPRM-5 (TPA) at different activation temperatures. This observation correlates well with the findings based on the analysis of the single component adsorption equilibrium data (see Figure 3.4) in which the CH_4 appears to adsorb onto a secondary pore system that arises from the high level of faulting. In the case of Sr^{2+} -UPRM-5 (TBA), CH_4 appears to undergo slightly smaller adsorption rates upon activation of the adsorbent at 180 °C as evidenced by the subtle shift of the fractional uptake curve in the mid to long time region. The same seems to happen to CO_2 when adsorbing into Sr^{2+} -UPRM-5 (TPA), only on a prominent fashion and within the 8-MR pore system instead of the secondary.

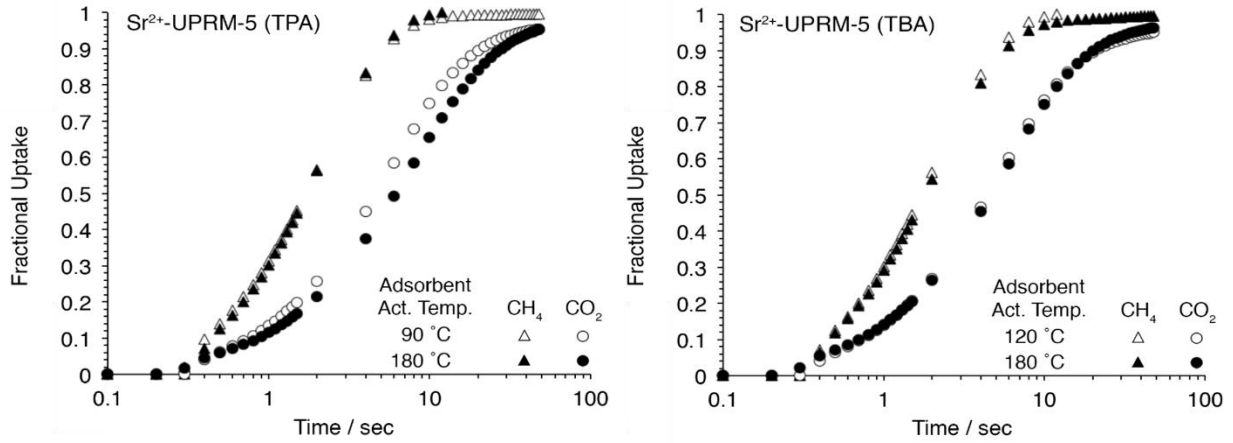


Figure 3.5 Experimental CO_2 and CH_4 fractional uptakes for Sr^{2+} -UPRM-5 (TPA) and Sr^{2+} -UPRM-5 (TBA). Data obtained at a temperature of 25°C and a gas pressure of 0.005 atm.

The experimental transient fractional uptakes were fitted against a phenomenological model to estimate diffusion time constants ($D L^{-2}$). This model included polydispersity of the adsorbent particle size. The base model employed was proposed by Ruthven for a finite volume system and slab shaped particles:⁴⁷

$$F = \frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{2\Lambda(1+\Lambda)}{1+\Lambda+\Lambda^2 q_n^2} \exp\left(\frac{-D q_n^2 t}{L^2}\right) \quad (3.2)$$

where F is the fractional uptake, M_t is the uptake at any time t , M_∞ is the final uptake as t approaches infinity, and $D L^{-2}$ is the diffusion time constant. The q_n series are the non-zero positive roots of:

$$\tan q_n = -\Lambda q_n \quad (3.3)$$

where Λ is the ratio of the volumes of the solution and the slab shaped particle. The following equation correlates the final fractional uptake to Λ :

$$\frac{M_\infty}{2aC_0} = \frac{1}{1+\Lambda} \quad (3.4)$$

where C_0 is the initial solute concentration in the volume and a is the length of the space between the solute volume wall and the slab shaped crystal.⁴⁸ The model shown in eq. 3.2 however, does not account explicitly for the effect of polydispersity in the adsorbent particle size. This is important since, for instance, Ruthven and co-workers have reported observation of significant differences among the predicted fractional uptakes when employing different size distribution parameters.^{49, 50} Here, we attempted to address this via incorporation of a particle size distribution (i.e, eq. 3.1) to eq. 3.2 based on data gathered from direct observations of particle sizes.

SEM micrographs (see Figure B.1 in Appendix B) gathered for the Sr^{2+} -UPRM-5 (TBA) and (TPA) variants, which show considerable size polydispersity among the crystals. The characteristic particle or crystal length was taken to be the longest dimension for a slab shaped crystal, L . The distribution of the crystal size was found to be well represented by a Gamma type distribution (see Appendix B). Since the statistical parameter μ/σ value was found to be less than 10 the crystal size polydispersity should not be neglected in the transport model,⁵⁰ and, therefore, the volumetric transport model shown in eq. 3.2 was modified as follows:

$$F = 1 - \sum_{n=1}^{\infty} \left(\frac{2\Lambda(1+\Lambda)}{1+\Lambda+\Lambda^2 q_n^2} \right) \int_{x=0}^{\infty} \exp \left(-(q_n)^2 \frac{Dt}{L_{ave} x^2} \right) \frac{1}{\beta^\alpha \Gamma(\alpha)} x^{\alpha-1} e^{\frac{-x}{\beta}} dx \quad (3.5)$$

Estimation of diffusion time constants was performed upon fitting of the volumetric transport models (eq. 3.5) against the mid to long time region of the experimental fractional uptake curves.

This was done to overcome the effect of adsorption in a bimodal pore system on the prediction of the CO₂ and CH₄ fractional uptakes. For instance, we have assumed that the portion of the fractional uptake that represents the CO₂ uptake in the 8-MR channels is the one in which the inflection toward approaching equilibrium begins (see Figure 3.5). It is assumed that 8-MR pores will take more time to be filled due to surface and kinetic restrictions associated with the dimension of these channels. This consideration, however does not overcome the effect of a bimodal system pores when the adsorbent surface is nearly empty (i.e., at low pressures). As observed in Figure E.1 (A), there is a small under-prediction of uptakes at mid-range times, and a small over-prediction of the uptakes observed at longer times. Meanwhile, Figure E.1 (B) shows a good adjustment at short times, but also an over-prediction after ca. 2 seconds. However, the latter disappears at longer times.

Tables F.1 and F.2 show diffusion time constant ($D \text{ L}^{-2}$) values for CO₂ and CH₄ estimated using fits of the transport model shown in eq. 3.5 and different pressures. These values are in the same order as those that have been reported for the adsorption of light gases onto ETS-4, including CH₄.²⁶ As stated above, the UPRM-5 adsorbent variants were pre-activated at temperatures where the surface areas are known to be the greatest and the structures have suffered no collapsing:³² at 90°C for Sr²⁺-UPRM-5 (TPA) and 120°C for Sr²⁺-UPRM-5 (TBA). In addition, diffusion time constants were also estimated using gas fractional uptakes gathered for both UPRM-5 variants activated at 180°C to establish a better correlation between framework contraction and kinetic adsorption selectivity, if any. Tables F.1 and F.2 also show the residual root mean square errors (RRMSE) and the average relative errors (ARE) for fits between the fractional uptakes and the volumetric transport models.^{51, 52}

Adsorption onto Sr²⁺-UPRM-5 (TPA) and Sr²⁺-UPRM-5 (TBA) exhibited diffusion time constants that increase with an increase in gas pressure, which is expected since in the concentration gradient toward the surface is decreasing as the loading is increased. The ARE and RRMSE values calculated for fits of fractional uptakes of CH₄ onto Sr²⁺-UPRM-5 (TPA) are significantly smaller than those calculated for CO₂ suggesting that the adsorption of CH₄ in the 8-MR pore system is negligible. CO₂ molecules also seem to diffuse through both pore systems, but with restrictions probably associated to the presence of residual Na⁺ and linked structural water, and possible blockage of the pore channels by other CO₂ adsorbed molecules.^{33, 39, 53}

3.4.5 CO₂ Selectivity Kinetic Selectivity

For preliminary assessment of the selectivity of Sr²⁺-UPRM-5 (TPA) and Sr²⁺-UPRM-5 (TBA) toward CO₂ over CH₄, the kinetic selectivity was calculated using the following expression:

$$\frac{K_{H,CO_2}}{K_{H,CH_4}} \left(\frac{D_{CO_2}}{D_{CH_4}} \right)^{1/2} \quad (3.6)$$

where K_H is the Henry's law constant.^{33, 54} Table F.3 shows Henry's law constants calculated from the adsorption equilibrium data shown in Figure 3.4. Meanwhile, Figure 3.6 shows the resulting kinetic selectivity values at selected pressures. At an activation temperature of 180°C, both UPRM-5 variants show smaller CO₂ selectivity values, probably due to thermal framework contraction that may be limiting the access to adsorption sites located within the 8-MR channels. This correlates with what was suggested by the MAS NMR data, which showed shifting of the resonances associated with movement of the semi-octahedral titanium centers upon dehydration and, therefore, may cause extra-framework cations (i.e., adsorption sites) to move as well and become less accessible.^{26, 44}

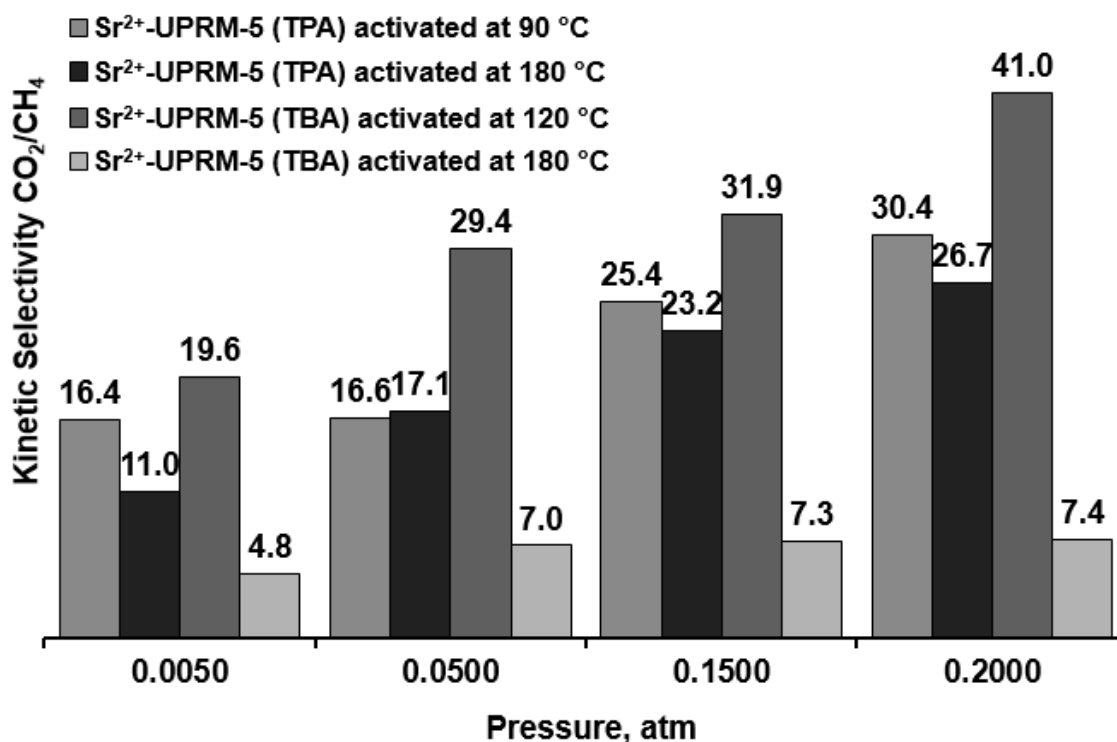


Figure 3.7 CO₂/CH₄ kinetic selectivity of Sr²⁺-UPRM-5 (TPA) and Sr²⁺-UPRM-5 (TBA) calculated at 25 °C, different adsorbent activation temperatures, and average gas pressure.

Table 3.1 shows single point equilibrium, intrinsic and kinetic selectivity values, as well as diffusion time constant ratios for selected adsorbents, including carbons, zeolites and MOFs. The largest equilibrium CO₂ selectivity among the adsorbents presented here were MOF-5 (~15), followed by Sr²⁺-UPRM-5 (TBA) (~8.0) and Sr²⁺-UPRM-5 (TPA) (~8.0). The largest intrinsic CO₂ selectivity corresponds to Sr²⁺-UPRM-5 (TBA) (~42). However, the combination of all these elements, all unified in the kinetic selectivity, seems to benefit the Sr²⁺-UPRM-5 variants. Furthermore, the data shown in Table 3.1 considers only cases with similar CO₂ and CH₄ concentrations due to scarcity of data that represents conditions perhaps more representative of natural gas mixtures.

Table 3.1 Pure component CO₂/CH₄ adsorption selectivity and diffusivity values reported for selected adsorbents.

Adsorbent	Temperature (°C)	Single Point Equilibrium Selectivity (-) [*]	α_{CO_2/CH_4}^{**}	Maximum Reported D_{CO_2}/D_{CH_4} (-)	Maximum Kinetic Selectivity (-) ^{***}	Reference
Sr ²⁺ -UPRM-5 (TPA) Act. @ 90 °C	25	8.04	39.86	0.58	30.43	This work
Sr ²⁺ -UPRM-5 (TBA) Act. @ 120 °C	25	8.05	42.34	0.94	41.04	This work
Sr ²⁺ -ETS-4 Act. @ 100 °C	50	1.33	1.69			Cavenati et al. ²⁶
Cu-MOF	25	1.86	4.90	26.05	25.03	Bao et al. ²⁰
MIL-101 (Cr)	30	4.67	19.69			Munusamy et al. ⁵⁵
Mesoporous Carbon	25	2.91	4.82	1.84	6.54	Saha and Deng ⁵⁶
Zeolite 5A	25	5.19		0.47	3.6	Rufford et al. and Saha et al. ^{6, 56}
MOF-177	25	7.05	5.72	1.58	7.18	
MOF-5	25	14.81	14.34	0.64	11.50	
SSZ-45	30	5.22	11.47			Smeets et al. ⁵⁷
Ordered Mesoporous Carbon	25	2.25	2.50	0.47	1.72	Yuan et al. ⁵⁸
Zeolite-13X	25	4.34	13.21			McEwen et al. ⁷
ZIF-8	25	3.09	3.13			

*Single Point Equilibrium Selectivity = $\frac{q_{CO_2}}{q_{CH_4}}$ @ 1 atm; **Intrinsic Selectivity: $\alpha_{CO_2/CH_4} = \frac{K_{H,CO_2}}{K_{H,CH_4}}$; ***Kinetic Selectivity = $\frac{K_{H,CO_2}}{K_{H,CH_4}} \left(\frac{D_{CO_2}}{D_{CH_4}} \right)^{1/2}$

Table 3.2 Pure component CO₂/CH₄ kinetic selectivities calculated at 25 °C for a hypothetical mixture of 4% of CO₂ and 96% of CH₄.

Adsorbent	$D L^{-2}$ for CO ₂ at 4% (s ⁻¹)	$D L^{-2}$ for CH ₄ at 96% (s ⁻¹)	Kinetic Selectivity
Sr ²⁺ -UPRM-5 (TPA) Act. @ 90 °C	0.42	1.57	20.68
Sr ²⁺ -UPRM-5 (TBA) Act. @ 120 °C	0.31	1.80	17.68

Table 3.2 shows kinetic selectivity values estimated for a 4% CO₂ / 96% CH₄ hypothetical mixture - representative of the presence of CO₂ in natural gas – based on single component data. Since a kinetic selectivity greater than 12 has been considered as appropriate for gas separations in pressure swing adsorption (PSA) systems,²⁰ the data shown in Table 3.2 confirms the potential use of Sr²⁺-UPRM-5 (TPA) and Sr²⁺-UPRM-5 (TBA) for the removal of CO₂ from natural gas effluents. Furthermore, these Sr²⁺-UPRM-5 variants exhibit equilibrium working capacities (Figure 3.4) larger than those of ETS-4³⁵ at conditions similar to those that have been reported for the removal of CO₂ from coal bed methane using the Molecular Gate. UPRM-5 materials may provide a pathway for the improvement of for separations based on PSA with flexible titanium silicates. However, more tests are needed to elucidate the effect of multi-cycle adsorption, tolerance to exposure to water vapor as well as the development and optimization of appropriate regeneration schemes.

3.5 Concluding Remarks

Thermally induced structural changes in Sr²⁺-UPRM-5 (TPA) and Sr²⁺-UPRM-5 (TBA) adsorbents were analyzed via *in situ* techniques. *In situ* XRD and careful indexing showed orthorhombic crystal structures and lattice parameters similar to Zorite that remained upon dehydration even at high temperatures. The data also revealed that the 8-MR pore system in these materials is the most susceptible to contraction during thermal treatment in comparison to the pore system related to faulting. This might explain the differences in CO₂ and CH₄ adsorption loadings under equilibrium as well as diffusion rates. *In situ* ²⁹Si MAS NMR confirmed the important role of the semi-octahedral titanium centers in the thermal contraction process.

Sr²⁺-UPRM-5 (TPA) and Sr²⁺-UPRM-5 (TBA) adsorbents were also analyzed to determine their capacity for kinetic separation of the CO₂/CH₄ pair at ambient temperature. Kinetic selectivities

values for CO₂ over CH₄ at an activation temperature of 120°C reached a maximum of ca. 41 in the case of Sr²⁺-UPRM-5 (TBA) and ~30 for Sr²⁺-UPRM-5 (TPA). For a hypothetical mixture of 4% CO₂/ 96% CH₄, the kinetic selectivity observed for the TPA adsorbent variant was ca. 20. The results show the potential of using Sr²⁺-UPRM-5 like materials as molecular sieves for PSA systems in the separation of CO₂/CH₄. However, fixed bed dynamic adsorption tests should be further performed to determine long-term reusability and bed diffusion performance for CO₂ in Sr²⁺-UPRM-5 (TPA) and Sr²⁺-UPRM-5 (TBA).

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Chapter 4

Removal of Carbon Dioxide from Gas Mixtures Using Sr^{2+} -UPRM-5 Fixed Beds Under Dynamic Conditions and a Thermal Treatment Study for Re-activation between Adsorption Cycles

4.1 Chapter Summary

Sr^{2+} -UPRM-5 (TPA) and Sr^{2+} -UPRM-5 (TBA) beds were assembled to study the adsorption of CO_2 from N_2 under dynamic conditions. Adsorbed amounts calculated from bed outlet concentration profiles were similar to those achieved under equilibrium conditions in the case of Sr^{2+} -UPRM-5 (TBA) and smaller in the case Sr^{2+} -UPRM-5 (TPA) perhaps due to diffusional transport limits. Measurements of bed usage efficiency from the Mass Transfer Zone model also confirm this, with an average bed use of 77% for Sr^{2+} -UPRM-5 (TBA) and 65% for Sr^{2+} -UPRM-5 (TPA). A combined mass transport phenomenological and Linear Driving Force (LDF) mass transfer rate model was used to predict fixed bed outlet concentration profiles. The model made good predictions of breakthrough points but, in some cases, failed to describe the “tailing” portion of the profiles. The latter might be due to the presence of a dual system of pores in Sr^{2+} -UPRM-5. Thermal activation between cycles showed to be detrimental to CO_2 adsorption working capacities. Lowering of the system pressure, on the other hand, results to be sufficient to achieve full regeneration of the material. This could be advantageous in terms of energy use efficiency in large scale applications. Based on these results, its potential for air revitalization of closed volume environments was also evaluated.

4.2 Introduction

Pressure/vacuum swing adsorption (PSA/VSA) is one of the most feasible technologies for CO_2 separation and release for further sequestration at large scale. The VSA stage allows for

regeneration of the adsorbent by reducing the total pressure of the system and, therefore, releasing the CO₂; the total pressure of the system “swings” between high pressures in feed and low pressures in regeneration.¹⁻⁴ PSA has been identified as a promising method due to ease of implementation and low cost of operation, compared to other CO₂ capturing methods such as cryogenic separations.^{5, 6} Two factors have been found to be of great importance for the implementation of PSA technology: the adsorbent and the engineering design of the PSA unit. However, in principle, the adsorbent is the most important part of the PSA unit, so even when the engineering design is optimized, if the adsorbent lacks of the required characteristics for the application, the system will be considered inefficient.^{2, 7} Therefore, many efforts are been focused on the development of adsorbents which can make PSA systems effective.

The adsorbents that have been the most widely studied for this purpose are zeolites, particularly 4A, 5A and 13X due to high selectivity and fast CO₂ diffusion.^{8, 9} These materials have been found their way into non-CO₂ emission applications that focus instead on air revitalization in close volume environments. Such is the case of the Carbon Dioxide Removal Assembly (CDRA) used at the International Space Station (ISS), where the CO₂ levels need to be kept at ppm levels.^{4, 10} Materials such as metal-based adsorbents, carbon molecular sieves, and activated carbons have been also carefully investigated and develop in specific PSA systems for commercial purposes.² Despite the successes in using the aforementioned materials in PSA technology, there is significant room of improvement when it comes to increasing working capacity while aiming a better selectivity per cycle. Flexible titanium-silicates could offer an answer to this.

As mentioned in previous chapters, ETS-4 has shown to be highly selective towards CO₂¹¹ because of its pore size tailoring capability. Pore sizes in ETS-4, which range from 3-4 Å, can be easily adjusted upon thermal dehydration. This allows for separation of gas mixtures where the

dimensions of the adsorbates are very similar such as CO₂, CH₄ and N₂ mixtures.^{12, 13} ETS-4 has been used as the key component of a PSA commercial application named “Molecular Gate® Adsorption Technology”, from Guild Associates, Inc.^{1, 14} However, the setup still requires several cycles to achieve the desired production targets due to relatively low working capacities.

UPRM-5 is another flexible titanium-silicate with this “tuning” capability, but with less impact on working capacity. As presented in chapters 2 and 3 of this work, this material has shown to display remarkable selectivity toward CO₂. This is all possible due to the incorporation of quaternary ammonium cations, TEA, TPA and TBA, as structure directing agents (SDAs) during the synthesis of the material.^{15, 16} The use of these SDAs leads to materials with different levels of random structural faulting, which impart each UPRM-5 variant with specific surface characteristics as well as thermal stability. Paired with surface functionalization, UPRM-5 offers an adsorbent with unique properties that could allow for CO₂ removal under a wide range of conditions.¹⁵⁻¹⁸

Recent static adsorption studies have shown the potential of UPRM-5 to be used as adsorbent for kinetic based separations.^{1, 2} For instance, Yu et al. gathered fractional uptake and equilibrium adsorption data for Sr²⁺-UPRM-5 (TEA) that suggest that N₂ and CH₄ could be separated upon careful thermal activation, resulting this in selectivity toward N₂, like in ETS-4, but with significant larger capacities.¹⁹ Most adsorbents, including traditional zeolites, always display better selectivity toward CH₄ instead. Likewise, chapter 3 showed that Sr²⁺-UPRM-5 (TPA) and Sr²⁺-UPRM-5 (TBA) variants are potential options for kinetic separation of CO₂ and CH₄.²⁰ Despite all of these findings, UPRM-5 has not been tested under dynamic adsorption conditions (i.e., fixed bed configurations).

This chapter presents a study of the separation of CO₂ from CO₂/N₂ mixtures in Sr²⁺-UPRM-5 (TPA) and Sr²⁺-UPRM-5 (TBA) fixed beds. The CO₂ bed inlet concentration was varied within

the 500 - 10000 ppm range to elucidate the performance of UPRM-5 in light of applications that include air rejuvenation in close volume environments and purification of natural gas.^{20, 21} A phenomenological transport model was developed to predict the CO₂ bed outlet concentration transient profiles and to describe the dynamics of the separation process. In addition, since adsorbent regeneration is an important step to every PSA system, an analysis of the material re-activation between cycles was also included. Finally, as a result of this assessment, the potential of these materials for the air revitalization of closed volume environments was also evaluated.

4.3 Experimental Procedure

4.3.1 Synthesis and Pelletizing of Sr²⁺-UPRM-5 (TPA) and Sr²⁺-UPRM-5 (TBA)

Sr²⁺-UPRM-5 (TPA) and Sr²⁺-UPRM-5 (TBA) were prepared using the procedures already reported elsewhere.¹⁵ Convective instead of microwave assisted heating was employed here in order to produce amounts of adsorbent suitable for fixed bed tests. A temperature of 180°C was used along with a crystallization period of 12 days. The resulting powdered materials (i.e., TPA- and TBA-UPRM-5) were recovered via vacuum filtration, washed with copious amounts of distilled/deionized water and carefully dried in a forced convection oven at 60 °C for 18 h. The samples were then detemplated via ion exchange with NH₄⁺ followed by exchange with Sr²⁺ cations, using NH₄Cl and SrCl₂ aqueous solutions, respectively. Pellets of these materials were obtained via compression of powders with a punch and a hydraulic press at a pressure of up to 2500 lbs, followed by crushing, and sieving through a mesh size of 0.841–0.420 mm. The presence of the unaltered phase of UPRM-5 in the pellets as well as crystallinity were verified by X-ray diffraction.

4.3.2 Material Characterization: Adsorption Equilibrium Isotherms and Thermo-Gravimetric Analysis (TGA)

Single-component equilibrium adsorption data for CO₂ and N₂ in pelletized UPRM-5 were gathered volumetrically using a Micromeritics ASAP-2020 unit at 25 °C and pressures up to 1 atm. Standard activation of the samples consisted of thermal treatment at 90°C and 120°C for Sr²⁺-UPRM-5 (TPA) and Sr²⁺-UPRM-5 (TBA), respectively, under vacuum for 18 h for the samples used for the fitting of the adsorption isotherm. The equilibration time to reach each equilibrium datum was at least 30 s. For re-activation analysis between cycles, the thermal treatment was performed at 100°C and 130°C for Sr²⁺-UPRM-5 (TPA) and Sr²⁺-UPRM-5 (TBA), which are the temperatures that were also used during fixed bed regeneration.

In order to determine the effect of sample re-activation on the CO₂ equilibrium adsorption performance, two different re-activation procedures were followed. The first one consisted of the consecutive collection of adsorption equilibrium isotherms using an adsorbent that was sequentially re-activated after being spent. The second one employed thermal/vacuum treatment only before the first adsorption cycle, and using vacuum assisted desorption without any thermal input between the remaining cycles.

Thermo-gravimetric analyses (TGA) were performed for Sr²⁺-UPRM-5 (TPA) and Sr²⁺-UPRM-5 (TBA) with a high-resolution TA-Q500 system at constant temperature, i.e. the activation temperatures, using a dry helium atmosphere at a constant flow of 48 mL min⁻¹ for 24 hrs.

4.3.3 Dynamic Adsorption Experimental Setup

A schematic for the experimental setup employed for the dynamic adsorption tests is shown in Figure 4.1.

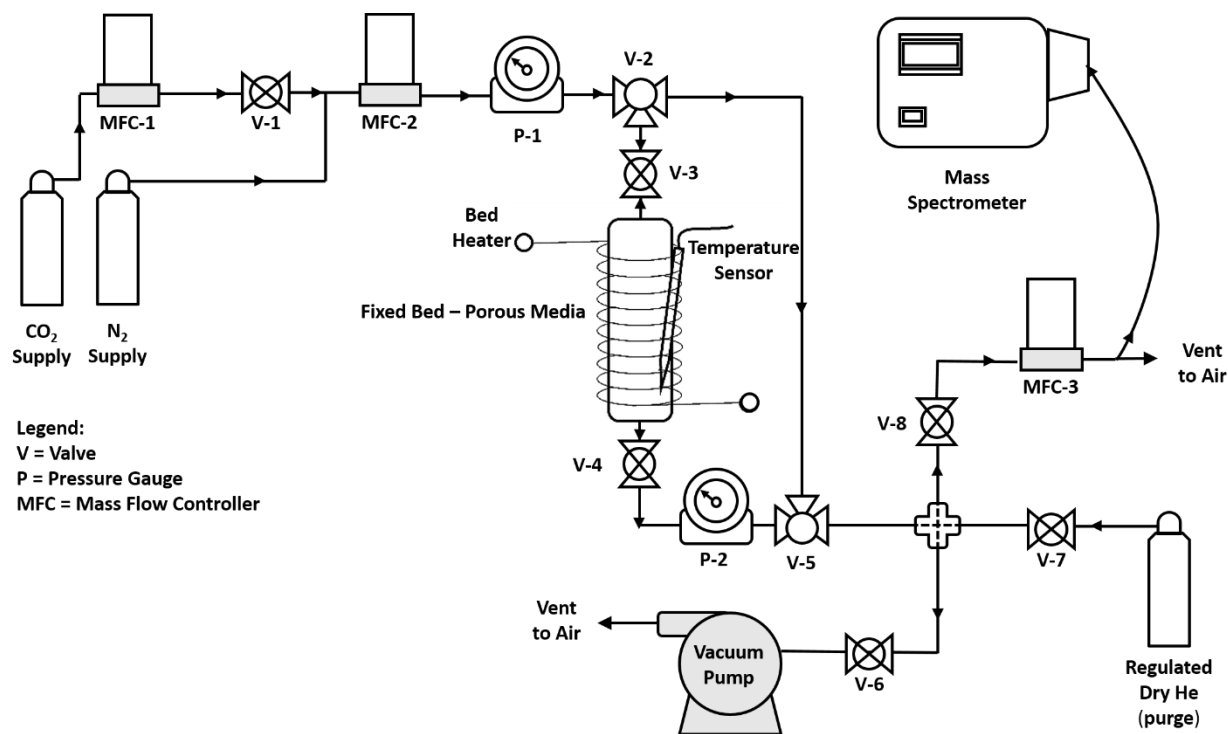


Figure 4.1 Schematic of the dynamic adsorption experimental set-up

4.3.3.1 Experimental Apparatus Components

A Hidden Analytical Mass Spectrometer was used to measure the CO₂ and N₂ bed outlet concentration in treated CO₂/N₂ mixtures. A 247D-A Channel Readout as well as three MKS mass flow controllers (MFC) were used to obtain precise flow delivery control and reading (0 to 1000 sccm). Two pressure gages were used to monitor the pressures in gas lines. Calibration of each of the aforementioned instruments was performed before every experiment. In Figure 4.1, valves V-1 and V-6, V-7 and V-8 represent ball valves. V-3 and V-4 are vacuum ball valves, and V-2 and V-5 are manual three-way valves.

4.3.3.2 Experimental Apparatus Set-up

Adsorbent activation consisted of thermal treatment of the bed at 100°C and 130°C of Sr²⁺-UPRM-5 (TPA) and Sr²⁺-UPRM-5 (TBA) while applying vacuum for 18 hrs prior the first adsorption cycle. Then, for each of the consecutive cycles, only vacuum was applied to the packed bed for 18 hrs prior to each analysis. For this purpose, it was necessary to close valves V-3, V-7 and V-8,

open valves V-4 and V-6, and direct the V-5 three-way valve toward the vacuum pump. Upon activation, a helium purge was achieved by closing V-6 and opening V-7 until the pressure in the bed reached 1 atm, for about 1 min.

Before each experiment, N₂ flow was directed through V-2 and V-5 to MFC-3 and to the mass spectrometer. Stabilization of this gas flow was monitored for c.a. 60 minutes until the CO₂ concentration (c.a. 100 ppm) in the system background is stable. Afterward, the desired CO₂/N₂ mixture was directed to the mass spectrometer for calibration by setting the corresponding flows in MFC-1 and MFC-2. The adsorption experiment was then started by opening V-3 and V-4, and directing V-2 and V-5 toward the bed, allowing the treated flow to be analyzed by the mass spectrometer. The system pressure in each experiment was close to atmospheric.

4.3.3.3 Sr²⁺-UPRM-5 (TBA) and (TPA) adsorption bed.

The stainless steel column housings length and diameter were 0.123 and 0.0104 m. The gas flow was set to 250 sccm, for a residence time in the packed bed of ≈ 3 seconds, allowing for a fully developed flow profile. To avoid losing packing of the material and minimizing dusting of the system flow lines, stainless steel springs and screens were used at both ends of the column. The amount of adsorbent in the column was weighted after the experiments. The kinetic adsorption capacity at breakpoint was obtained by,

$$q_b = \frac{y_{CO_2} \rho_{gas} V_{total}}{MW_{gas} m_{adsorbent}} \int_0^{t_b} \left(1 - \frac{C(t)}{C_i}\right) dt \quad (4.1)$$

where q_b is the carbon dioxide adsorbed mass per mass of adsorbent at the breakpoint time t_b , is y_{CO_2} the CO₂ molar fraction, V_{total} is the total volumetric flow, MW_{gas} is the gas molecular weight, $m_{adsorbent}$ is the adsorbent mass, ρ_{gas} is the gas density, and the $C(t)$ and the C_i , the outlet and inlet concentrations, respectively. The integral part in the above equation was obtained by estimating the area under the $\left(1 - \frac{C(t)}{C_i}\right)$ transient profile.

4.3.4 Modeling of Bed Outlet Gas Concentration Profiles

A mass balance was the base of the mathematical model used to describe the CO₂ adsorption fixed-bed dynamics. A constant volumetric gas flow rate along the bed was also assumed since the CO₂ present in the mixtures were in trace amounts compared to N₂. A negligible bed pressure drop was assumed, too. Heat generated by the CO₂ adsorption was neglected since previously reported isosteric heat of adsorption values are below 43 kJ/mol for both UPRM-5.¹⁵ The following additional assumptions were employed to process the model:

- (i) The gas flow velocity profile could be described by the axially dispersed plug flow model;
- (ii) The mass transfer rate is represented by a linear driving force (LDF) model;
- (iii) The gas phase behaves as an ideal gas mixture;
- (iv) Radial concentration and temperature gradients are negligible; and
- (v) Negligible pressure drop along the system.

The mass balance at any axial position along the column for each component is given by eq. 4.2 and the initial and boundary conditions are presented in eq. 4.3-4.5.

$$\frac{\partial Y_i(z,i)}{\partial t} = D_L \frac{\partial^2 Y_i(z,i)}{\partial z^2} - \frac{u \partial Y_i(z,i)}{\varepsilon_{bed} \partial z} - \rho_{particle} \left(\frac{1-\varepsilon_{bed}}{\varepsilon_{bed}} \right) \left(\frac{RT_{feed}}{P_{feed}} \right) \frac{\partial q_i(z,i)}{\partial t} \quad (4.2)$$

Boundary conditions:

$$\text{B.C. 1: } Y_i(z, i) = Y_{feed} \quad \text{at } z = 0; \quad (4.3)$$

$$\text{B.C.2: } \frac{\partial Y_i(z,i)}{\partial z} = 0 \quad \text{at } z = L; \quad (4.4)$$

$$\text{B.C.3: } Y_i(z, i) = q_i(z, i) = 0 \quad \text{at } t = 0; \quad (4.5)$$

where u is the superficial velocity, Y_i is the gas phase mole fraction for component i , q_i is the adsorbed amount, R is the gas constant, T is the temperature, P is the total pressure, $\rho_{particle}$ is the

particle density, ε_{bed} is the bed void fraction, and D_L is the axial dispersion coefficient, which may be estimated by the following equation:

$$D_L = 0.7D_m + 2r_p u \quad (4.6)$$

where r_p is the average radius of particle, D_m is the molecular diffusivity, which may be calculated from the Chapman-Enskog kinetic theory. The mass transfer rate was estimated using a type linear driving force (LDF) model:

$$\frac{\partial q_i}{\partial t} = \frac{15D_e}{r_p^2} (q_i^*(z) - q_i(z)) \quad (4.7)$$

where r_p is the radius of particle, q_i^* is the equilibrium adsorption amount for component i , and D_e the effective pore diffusivity. The D_e can be calculated as follow,

$$D_e = \frac{\varepsilon_{particle}}{\tau} \frac{D_s D_m}{D_s + D_m} \quad (4.8)$$

where $\varepsilon_{particle}$ is the particle void and τ is the particle tortuosity. D_s is the intracrystalline pore diffusivity.

Equilibrium adsorption data were estimated using the Modified Dubinin-Ashtakov (MDA) equation since the materials have shown to have a heterogeneous surface and linear interactions at low pressures typical of Langmuir type isotherms.

$$q_i^* = q_0 \left[\beta_1 \exp \left[- \left(C \ln \left(\frac{P_0}{P} \right) \right)^{n_1} \right] \right] + \beta_2 K P \quad (4.9)$$

where β_1 , β_2 , C and K are defined by:

$$\beta_1 = 1 - \exp \left(-\alpha \frac{P}{P_0} \right) \quad (4.10)$$

$$\beta_2 = \exp \left(-\alpha \frac{P}{P_0} \right) \quad (4.11)$$

$$C = \frac{RT}{\sigma E} \quad (4.12)$$

$$K = \frac{q_1}{P_0} \quad (4.13)$$

and q is the adsorbed amount, q_o is the saturated adsorbed amount, α is a fitting parameter, P is partial pressure, P_o is the saturated vapor pressure of the adsorbate, R is the universal ideal gas constant, T is the absolute temperature, σ is the adsorbate affinity coefficient, E is the characteristic adsorption energy and K is the Henry's law constant.

Eq. 4.2 together with the equilibrium isotherm model (eq. 4.9) were solved simultaneously using the Orthogonal Collocation in Finite Elements Method (OCFEM). The computer software suite gPROMS was used for this task. Table 4.1 shows a summary of the parameters used. For practical purposes, properties such as particle void and tortuosity were taken from values reported for other titanium-silicates.^{22, 23} These properties are part of the terms involved in the effective diffusivity, so as D_s been the fitting parameter in the calculation, it is logic to conclude that the final estimation of D_s will also englobe the effect of these parameters, although these are not so critical as to change significantly the diffusivities results.²⁴

Table 4.1 Summary of parameters used for the modeling of CO₂/N₂ separation on a fixed-bed

	Sr ²⁺ -UPRM-5 (TPA)	Sr ²⁺ -UPRM-5 (TBA)
Bed length, (m)	0.123	
Bed inner diameter, (m)	0.0104	
ϵ_{bed}	0.628	0.703
ρ_{bed} , kg/m ³	724	750
Pellet diameter, (m)	0.0042-0.0085	
$\rho_{pellets}$, kg/m ³	2436.11	2013.94
ϵ_{pellet}	0.44	
τ	3	

4.4 Results and Discussion

4.4.1 Adsorbent Regeneration

Thermo-gravimetric data were gathered while soaking the adsorbent for a considerable length of time at a constant temperature (100 or 130°C). Figure 4.2 shows a persistent weight loss beyond 12 h for Sr²⁺-UPRM-5 (TPA) and Sr²⁺-UPRM-5 (TBA), respectively. This suggests that there is a

continuous removal of tenacious water from the semi-octahedral titanium centers in UPRM-5. This also induces further structural contraction that in turns causes a reduction in the adsorption capacity upon consecutive thermal re-activation, as found for other titanium silicates.^{12, 13, 25}

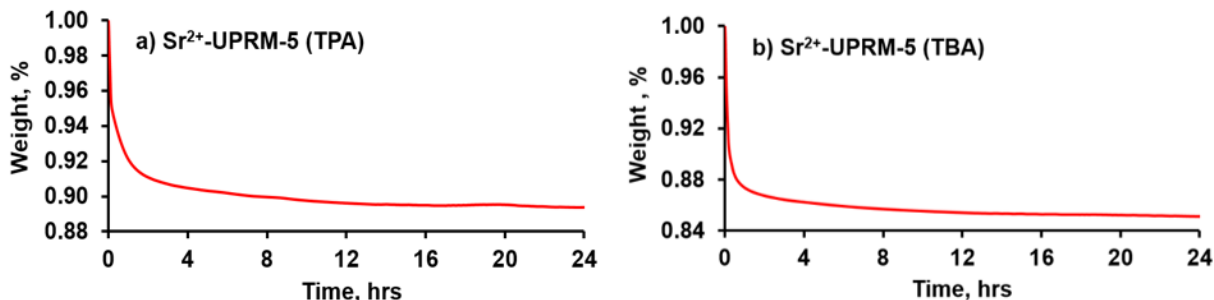


Figure 4.2 Thermo-gravimetric analysis of a) Sr^{2+} -UPRM-5 (TPA) at 100°C and, b) Sr^{2+} -UPRM-5 (TBA) and 130°C. Both gathered using a dry helium atmosphere

Single component adsorption isotherms were gathered to determine the effect of sample re-activation on the CO_2 equilibrium adsorption performance. Figure 4.3 shows adsorption isotherms gathered consecutively using a Sr^{2+} -UPRM-5 (TBA) adsorbent that was sequentially re-activated after being spent within each of the cycles. A reduction in adsorption capacity is evident from the results. A fourth isotherm was gathered after the adsorbent was exposed to ambient humidity for four days and then vacuum activated at 130°C. This isotherm shows a considerable recuperation in the CO_2 adsorption original capacity, especially at low pressures, which evidences the material's rehydration and, therefore, structural expansion.^{25, 26}

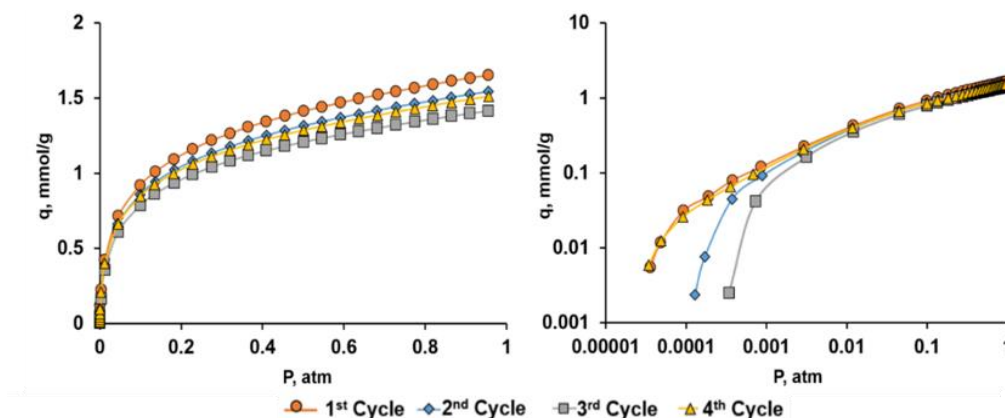


Figure 4.3 Single component CO_2 equilibrium adsorption isotherms gathered for Sr^{2+} -UPRM-5 (TBA) at 25°C. The sample was thermally and vacuum re-activated between cycles

In order to avoid the continuous structural contraction caused by thermal-reactivation between cycles, we employed vacuum assisted desorption without any thermal input between cycles. Applying this strategy for four continuous cycles showed no significant effect on the CO₂ adsorption working capacity of Sr²⁺-UPRM-5 (TBA) and Sr²⁺-UPRM-5 (TPA) (see Figure 4.4). There is a minimum increase in CO₂ loading amount after the first cycle at low pressures perhaps due to residual CO₂ being trapped within the adsorbent voids since the lowest pressure reached upon desorption was ca. 10⁻³ atm.

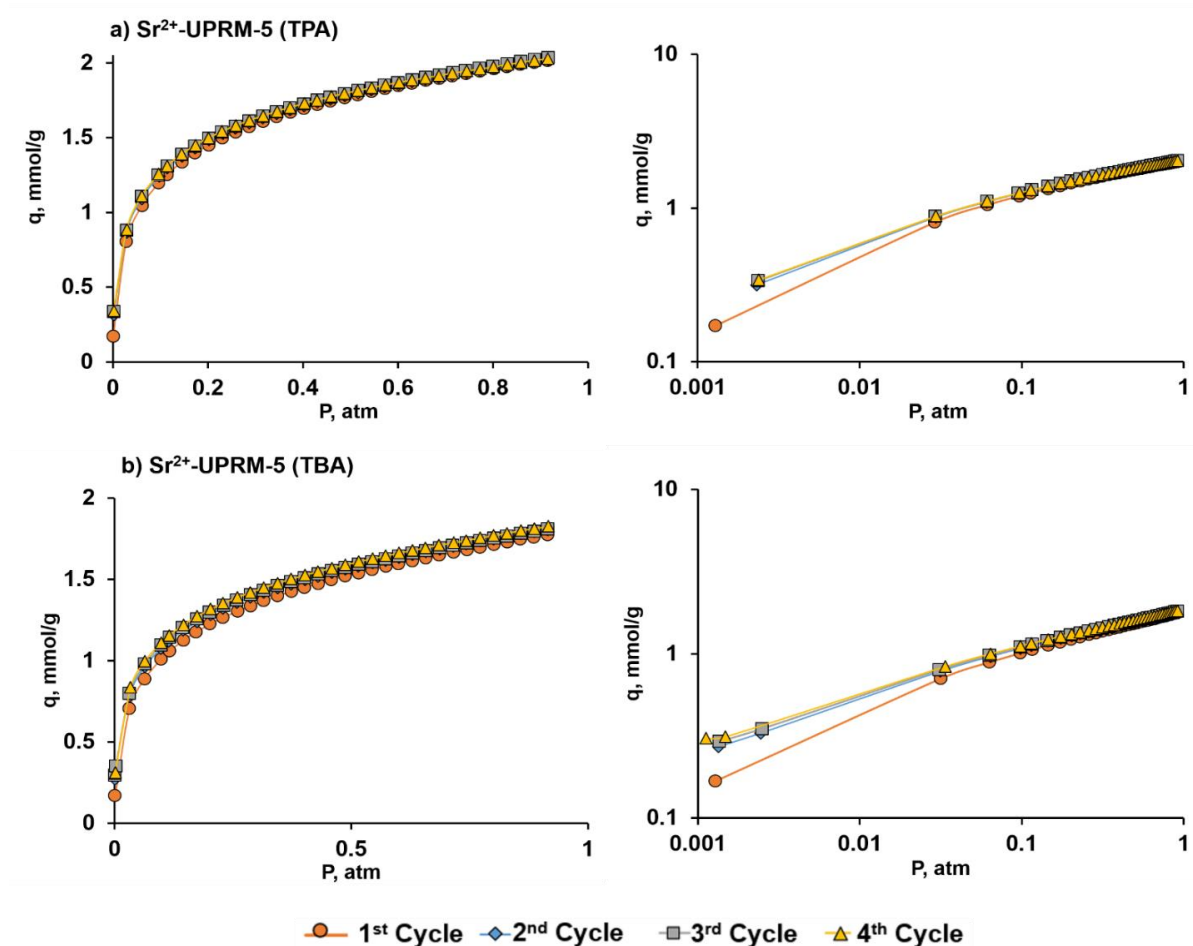


Figure 4.4 Single component CO₂ equilibrium adsorption isotherms gathered for Sr²⁺-UPRM-5 (TPA) and Sr²⁺-UPRM-5 (TBA) at 25°C. Each cycle began after a desorption pressure of ca. 10⁻³ atm was attained. The samples were not thermally activated between cycles. Desorption legs are not shown

The two methods for material re-activation (temperature/vacuum treatment vs. vacuum treatment) were also employed during the fixed bed experiments. For both series of experiments, the adsorbents were pre-activated (temperature/vacuum treatment) at the corresponding optimum temperature to tailor the pore size, i.e. 130°C, prior to the analyses. Results for four dynamic consecutive adsorption cycles are shown in Figure 4.5, for both methods of re-activation conditions, with an increase in feed concentration as follow: 1st cycle – 500 PPM, 2nd cycle – 1000 PPM, 3rd cycle – 5000 PPM and 4th cycle – 10000 PPM. It is evident that after the first cycle, the differences in breakthrough times become significantly larger as the material gets deteriorated with consecutive thermal treatment. This confirms that continuous thermal treatment applied to the Sr²⁺-UPRM-5 framework is detrimental to CO₂ adsorption working capacity; it is also evident that lowering the system pressure without thermal input suffices to effectively regenerate the material, as expected of any good PSA system.

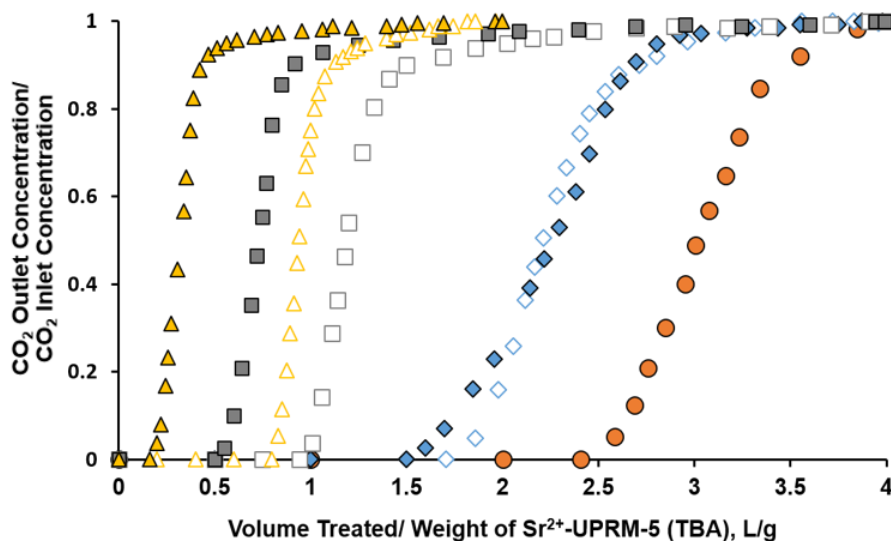


Figure 4.5 CO₂ Sr²⁺-UPRM-5 (TBA) bed outlet concentration profiles normalized by feed concentration of 500 (circles), 1000 (rhombus), 5000 (squares) and 10000 (triangles): solid markers represent the runs in beds thermally activated at 130°C under vacuum, while the open counterparts are for the consecutive runs with beds activated only under vacuum at room temperature. The first cycle started with the lowest concentration, i.e. 500 ppm; consecutive adsorption/regeneration cycles were performed with increasing feed concentration. Balance gas was dry N₂.

4.4.2 Bed Outlet Concentration Profiles

Extended fixed bed dynamic adsorption data were gathered for both, Sr^{2+} -UPRM-5 (TBA) and Sr^{2+} -UPRM-5 (TPA) (see Figures 4.6 and 4.7).

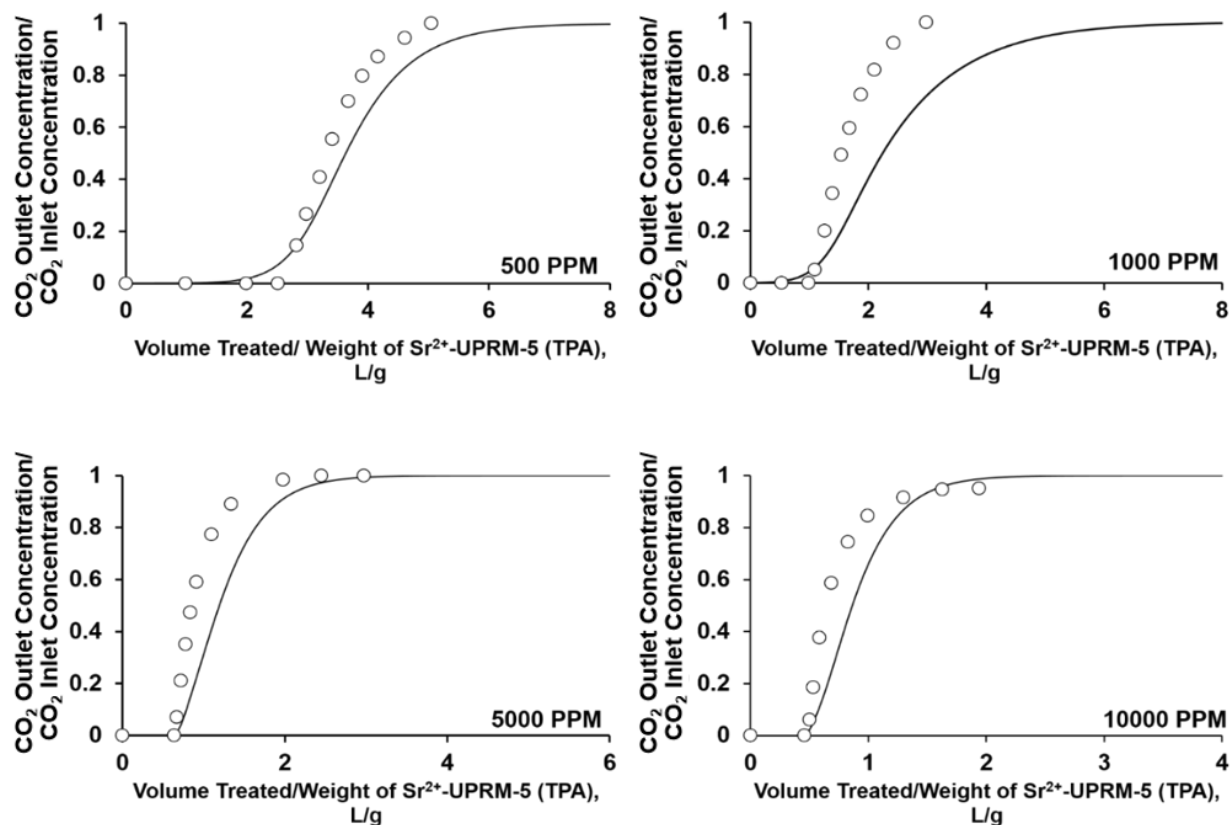


Figure 4.6 CO_2 Sr^{2+} -UPRM-5 (TPA) bed outlet concentration profiles normalized by feed concentration. Balance gas was dry N_2 LDF model prediction data represented by the circle markers.

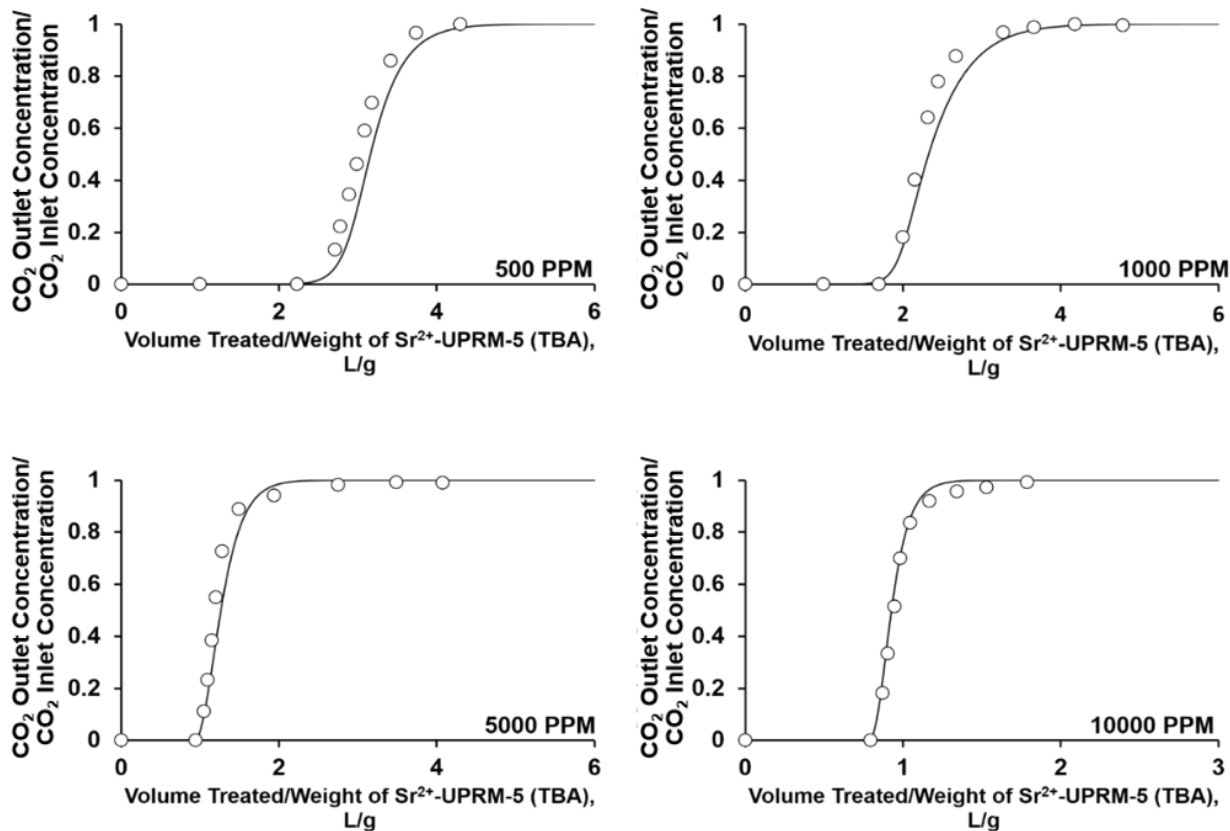


Figure 4.7 CO₂ Sr²⁺-UPRM-5 (TBA) bed outlet concentration profiles normalized by feed concentration. Balance gas was dry N₂ LDF model prediction data represented by the circle markers.

The resulting bed breakthrough or exhaustion times, t_b , are shown in Table 4.2. As expected, an increase in feed concentration will result in faster bed CO₂ breakthrough since a larger concentration gradient will saturate the column quickly.^{27 28} From the data shown in Table 4.2, it is evident that breakthrough times corresponding to Sr²⁺-UPRM-5 (TBA) are longer than the ones observed for Sr²⁺-UPRM-5 (TPA), with the exception of the 500 ppm inlet concentration case. The difference observed in the latter case may be due to significant adsorbent-adsorbate interactions at low pressures.^{15, 20}

Table 4.2 Summary of CO₂ adsorption data gathered using Sr²⁺-UPRM-5 (TPA) and Sr²⁺-UPRM-5 (TBA) beds.

Sr ²⁺ -UPRM-5 (TPA)	C ₀ , ppm	t _b , min	q _b , mmol/g	t _t , min	H _{UNB} /H _T , %
	500	79	0.06	108	26.5
	1000	30	0.04	50	40.0
	5000	19	0.13	28	32.3
	10000	14	0.19	23	39.2
Sr ²⁺ -UPRM-5 (TBA)	C ₀ , ppm	t _b , min	q _b , mmol/g	t _t , min	H _{UNB} /H _T , %
	500	72	0.05	92	21.5
	1000	51	0.07	67	24.4
	5000	29	0.20	39	25.8
	10000	24	0.33	30	19.3

The adsorbed amounts in the fixed bed bring also light onto what may be taking place across the column. It is observed for Sr²⁺-UPRM-5 (TBA) that the CO₂ adsorbed amounts at bed breakthrough point were approximately 70% of the total observed equilibrium amounts. However, the total adsorbed amounts calculated at complete bed saturation (i.e., CO₂ inlet concentration/CO₂ outlet concentration ~ 1), compare very well to the equilibrium adsorbed amounts. On the other hand, the adsorbed amounts at breakthrough for Sr²⁺-UPRM-5 (TPA) were ca. 40% of the CO₂ equilibrium adsorption data, while the total adsorbed amounts approximate to an average of only 70% of what was observed at equilibrium. This may be due to additional resistance brought by the bed design and adsorbent packing. For instance, residence time approximates to 2.5 s in the bed, much smaller than the observed equilibration times. Still, as shown in Figure 4.8, the CO₂ adsorption working capacities for Sr²⁺-UPRM-5 (TPA) and Sr²⁺-UPRM-5 (TBA) compare well to previously reported capacities for Sr²⁺-ETS-4 at low concentrations, and are superior at concentrations higher than 5000 ppm, which suggest potential use of these adsorbents for PSA systems for CO₂ removal.¹⁶

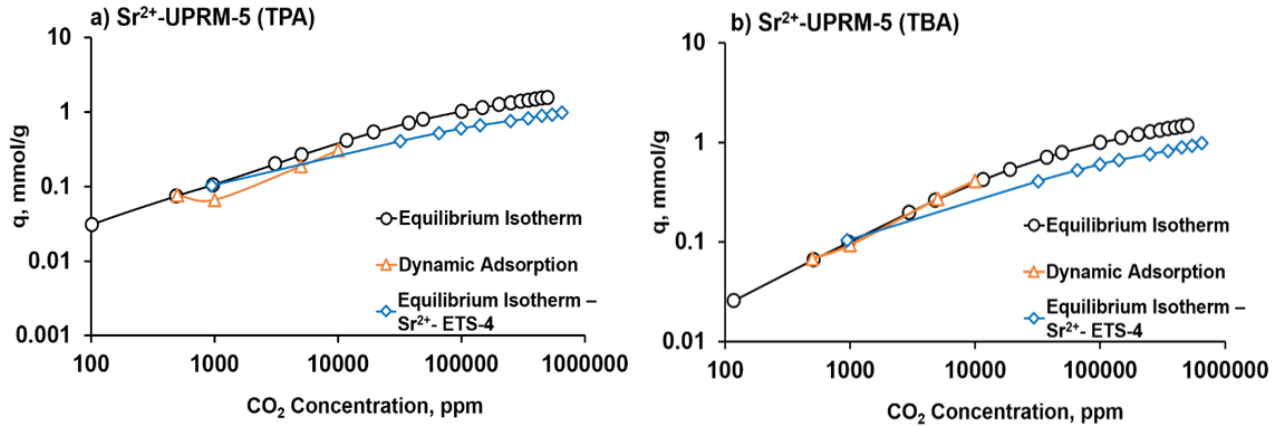


Figure 4.8 *CO₂ adsorption isotherms at 25°C for Sr²⁺-UPRM-5 (TPA) and Sr²⁺-UPRM-5 (TBA) pellets obtained via static volumetric and dynamic adsorption experiments*

Effectiveness of the columns were calculated using a Mass Transfer Zone model, (MZIP):

$$H_B = \frac{t_u}{t_t} H_T \quad (4.14)$$

$$t_t = \int_0^\infty \left(1 - \frac{c}{c_0}\right) dt \quad (4.15)$$

$$t_u = \int_0^{t_b} \left(1 - \frac{c}{c_0}\right) dt \quad (4.16)$$

where H_B is the bed used at break point, H_T is the total bed length, t_t is the time equivalent to the total or stoichiometric capacity and t_u is time equivalent to the usable capacity. The unused bed length, H_{UNB} , therefore can be defined as,

$$H_{UNB} = H_T - H_B \quad (4.17)$$

The unused bed percentage is in average 23% for Sr²⁺-UPRM-5 (TBA), while for Sr²⁺-UPRM-5 (TPA) is in the range of 26-40%. The latter values may suggest an undeveloped full flow profile impeding the formation of a sharp CO₂ concentration front along the bed. This could be due the bed design for which the H_T/D_i is slightly larger than 10.²¹ However, the small percentages of H_{UNB}/H_T of Sr²⁺-UPRM-5 (TBA) may suggest some kind of mass-transfer resistance due to intrinsic characteristics of Sr²⁺-UPRM-5 (TPA) rather than the bed design.

4.4.3 Modeling of Bed Outlet Concentration Profiles

The use of dynamic mathematical models are necessary to simulate processes of gas adsorption over time and to determine the behavior and potential of new adsorbents during adsorption-desorption cycles such as the ones present in PSA systems and for further optimization purposes.^{3,}

²⁹ The gProms application suite was used for this purpose, to simultaneously solve the differential equations involving the linear driving force (LDF) surface diffusion adsorption model. A surface diffusion mechanism is used when diffusion occurs through sufficiently small pores, so that the molecules can never escape the adsorbent force field. Therefore, internal mass transfer resistance is assumed to be limiting resistance factor.²⁹

Since the bed inlet concentration values correspond to the low-pressure range of an equilibrium isotherm, considered to be linear with high values of Henry's law constants, the LDF model is not applicable for the first 10 seconds of the model. A curvature was also observed in the isotherm for both, Sr²⁺-UPRM-5 (TPA) and Sr²⁺-UPRM-5 (TBA), which may counter-indicate the use of the proposed LDF model. An evaluation of the distribution factor K_d , which characterize this curvature was performed to verify the validity of the model. K_d can be approximated for Langmuir type isotherms, as $K_d = 1 + BP_0$, where B is the interaction parameter and P_0 is the adsorbate partial pressure. Defining the interaction parameter as $B = \frac{K}{q_0}$, K_d can be approximated for both adsorption isotherms to be ≈ 1 , for which the LDF model can be considered appropriate.³⁰

Figures 4.6 and 4.7 showed the bed outlet concentration profiles curves along with the theoretical curves calculated by the LDF model. Modeling of the curves shows good agreement with the experimental data up to t_b , (defined as the point in which a tangent line to the mass transfer zone intersects the horizontal axis). The modeling of the mass transfer zone, in the case of Sr²⁺-UPRM-5 (TPA), seems to be extended for longer period of time that what was observed experimentally.

This may be due to the fact that the predicted adsorption amounts by the adsorption isotherms where slightly higher than the obtained in a dynamic fashion, as shown in Figure 4.8.^{31, 32} Modeling of the mass transfer zone for Sr²⁺-UPRM-5 (TBA), on the other hand appears to be very accurate, especially at higher concentrations, but tends to deviate close to the bed exhaustion. This effect, called in the literature “tailing”, may indicate significant mass transfer resistance within the micropores.⁸ It will be discussed in more detailed shortly for both, Sr²⁺-UPRM-5 (TPA) and Sr²⁺-UPRM-5 (TBA).

The calculated superficial diffusion time constants are shown in Table 4.3. For both materials these are in the order of 10⁻¹⁰, been slightly higher for Sr²⁺-UPRM-5 (TBA) as expected from previous work. This was, because for Sr²⁺-UPRM-5 crystals, adsorption occur much faster through the 12-MR pores. However, due to presence of random faulting, some of these pore channels are “blocked” and most of the adsorption occur through the 8-MR pore rings, 3-4 Å in size, which allows kinetically driven separations. Chapter 3, explained that the amount of these faulting is higher for Sr²⁺-UPRM-5 (TPA), confining most of the adsorption to the 8-MR pore system.¹⁵⁻²⁰

Table 4.3 Diffusivity at different fixed bed feed concentrations.

	Sr²⁺-UPRM-5 (TPA)	Sr²⁺-UPRM-5 (TBA)
Concentration, PPM	D_s (m²/s)	
500	1.50E-10	6.50E-10
1000	1.10E-10	2.80E-10
5000	1.00E-10	1.80E-10
10000	0.75E-10	2.00E-10

Although this phenomenon is observed in the breakthrough curves of both Sr²⁺-UPRM-5 variants, it is more significant for Sr²⁺-UPRM-5 (TPA) in which the mass transfer zone extends for a wider range in the horizontal axis. Diffusivities appear to account for both, the faster and slower rates in which the two system of pores get saturated, causing the so called “tailing” near the bed

exhaustion.^{2, 8} Differences in the effective diffusivities indicate the adsorbent in which slower mass transfer rate is dominant, which as expected, is Sr^{2+} -UPRM-5 (TPA). The intrinsic complexity of the two pore systems present of Sr^{2+} -UPRM-5, represented an obvious limitation for accurately reproducing the “tailing” in the upper part of the mass transfer zone, as the model used can only average the transport coefficients occurring at the same time during the fixed bed adsorption.³³ Another consideration is that the model does not account for differences in the adsorbent surface potential, which may lead through a preferential flow pattern.³² Nevertheless, for design and potential evaluation purposes for future applications the presented results are valid and useful.

4.5 Evaluation for Possible Applications: Two Different Avenues

An evaluation for the prospective use of Sr^{2+} -UPRM-5 (TPA) and Sr^{2+} -UPRM-5 (TBA) in two potential adsorption applications for the removal of CO_2 are showed in this section. These are: 1) life supports systems for air revitalization of close volume environments, such as the Carbon Dioxide Removal Assembly (CDRA) at the ISS and, 2) for purification of natural gas for liquefaction processes. It should be clarified that these are not “case studies”, since this assessment is based in the results presented earlier and not in outcomes of experimental procedures adjusted to fulfill the system conditions of the applications for which the materials are evaluated. Therefore, the results that will be presented are just qualitative and should be taken as an indication of the feasibility of using Sr^{2+} -UPRM-5 to solve actual and realistic issues regarding CO_2 removal from gas mixtures. It should also serve as a benchmark in the design of further studies that look to use Sr^{2+} -UPRM-5 (TPA) and Sr^{2+} -UPRM-5 (TBA) to address these specific needs.

4.5.1 Revitalization of Closed Volume Environments

The CRDA at the ISS consist of four adsorption beds for the removal of water and CO₂. The silica gel/zeolite 13X bed is first used for the subtraction of water vapor of the inlet air. Then, the air is cooled and enters a zeolite 5A bed for CO₂ scrubbing. The treated air is re-humidified by going through the second desiccant bed and returned to the cabin. The fourth bed is also a zeolite 5A bed for CO₂ removal that is regenerated when the other one is in use. A complete cycle consists of the consecutive use of the two CO₂ scrubbing beds.³⁴⁻³⁶

The effectiveness of the CDRA is measured by two equations based on a human equivalent unit (HEU) with carbon dioxide partial pressures in the range of 0.0026 – 0.0051 atm (2.0 -3.9 mmHg). These are defined as follow:^{35, 36}

$$HEU \geq 1.723(pp\ CO_2, mmHg) - 0.37975 \quad (4.18)$$

The equivalent of 1 HEU is of 1 kg CO₂/day.

$$CO_2\ removal\ rate\ \left(\frac{lb}{hr}\right) \geq 0.158(pp\ CO_2, mmHg) - 0.035 \quad (4.19)$$

According to the second equation, the CO₂ removal rates for the given CO₂ partial pressure range, should be of 0.281-0.5812 lb/hr. A half-cycle last around 90 min, i.e. the use of one of the CO₂ scrubbers, and the mass flow of air entering the system is of 20.4 CFM. The bed is used in the first part of the breakthrough curve to the breakthrough point, which is defined according to their standards as CO₂% ≤ 0.01.³⁴

Sr²⁺-UPRM-5 (TPA) and Sr²⁺-UPRM-5 (TBA) were evaluated for the higher removal concentration of 5000 ppm under the conditions named above. For these results to be valid, the mass velocity of the fluid should remained constant, therefore the bed diameter was modified to retain this. Also, to accomplish the new breakthrough time the height of the column was also extended having in consideration the column efficiency percentages presented earlier.³⁷ The

resulting scale-up of the adsorbent column based on the requirements of the CDRA are described in Table 4.4.

Table 4.4 Proposed scale-up and column design to fit CDRA ISS operating conditions for Sr^{2+} -UPRM-5(TPA) and Sr^{2+} -UPRM-5(TBA).

Parameters	Sr^{2+} -UPRM-5 (TPA)	Sr^{2+} -UPRM-5 (TBA)
Mass Flow Velocity, (m/s)	0.049	
Half-Cycle Time, (min)	90	
Volumetric Flow, (CFM, m^3/s)	20.4, 0.01	
Diameter, (m)	0.500	
Length, (m)	0.433	0.315
Weight of Adsorbent, (kg)	63.880	44.740
Proposed CO_2 Removal (lb/hr)	0.76	0.76

The dimensions of the columns given in Table 4.4, corresponds to cylindrical beds. It also worth to mention that this adsorbent design meet the CO_2 removal rates required by the ISS, showing the potential of Sr^{2+} -UPRM-5 of operating at this conditions. The half-cycle time of the CDRA coincide with the amount of time needed to regenerate one of the CO_2 adsorbent beds. Therefore, further investigation should be performed to determine the minimum amount of time of system vacuum to fully regenerate the proposed packed bed. The use of mild temperatures i.e. less than 60°C , can be a possible solution to accelerate the re-activation process without further damaging of the Sr^{2+} -UPRM-5 framework. Determination of this temperature as well of heating methods to overcome heating transfer problems must be executed. CO_2 breakthrough curves at the actual CDRA's inlet volumetric flow and cycle time, should be effectuated to effectively compare the

results to zeolite 5A.³⁸ Also, changes in column design could be explored to maximize the column CO₂ removal efficiency.

4.5.2 Natural Gas Purification

Liquefaction of natural gas transforms the gas to a liquid state reducing significantly its volume, facilitating its transportation and broad use in a variety of markets.^{39, 40} The process requires low operating temperatures (<-160°C) in which the presence of CO₂ is detrimental due to freezing of this gas to solid state causing blocking of the lines and reduction of the system performance.⁴¹ Therefore the allowable concentrations of CO₂ in natural gas must be as low as 50 to 100 ppm.⁴² Good selectivity and adsorption capacity is then necessary to remove the large CO₂ levels found in natural gas.

The “Molecular Gate Technology” has shown to be effective for this purpose. It has shown also to purify natural gas effluents up to 50 ppm of CO₂ with an original concentration of 2% CO₂. The process conditions uses high pressures (100-600 psi) in addition of high volumetric flows (0.5-20 MM SCFD) and the adsorption-regeneration cycle has been described to last “a few minutes”.⁴³ The CO₂ breakthrough data presented in this work cannot account for a proposed design for the adsorbent column; specific experiments under these conditions should be performed. A possible design based in the large volume of natural gas can be proposed, but this system requires fast fluid velocities. Applying our velocity restriction in this case will result in nonrealistic and close to zero L/D ratios. Effective system and adsorbent column design should be done under in-plant systems conditions for a feasible proposal.

4.6 Concluding Remarks

In order to elucidate the potential of these materials for time-dependent CO₂ removal from N₂, dynamic concentration profiles at the bed outlet were obtained from Sr²⁺-UPRM-5 (TPA) and Sr²⁺-

UPRM-5 (TBA) fixed beds. The gathered results showed that at 500 ppm, Sr^{2+} -UPRM-5 (TPA) has a higher working capacity than Sr^{2+} -UPRM-5 (TBA). At higher concentrations, on the other hand, Sr^{2+} -UPRM-5 (TBA) exceeds considerably the adsorbed amounts of Sr^{2+} -UPRM-5 (TPA). It also shows sharper and steepest mass transfers zones than Sr^{2+} -UPRM-5 (TPA), which coincides with the results of MZP of an average of an unused bed performance of 23% for Sr^{2+} -UPRM-5 (TBA) and 35% for Sr^{2+} -UPRM-5 (TPA). This behavior can be attributed to the higher CO_2 diffusional mass transfer resistance in Sr^{2+} -UPRM-5 (TPA). As previously stated, this could be due to higher amount of structural faulting present in Sr^{2+} -UPRM-5 (TPA) relative to Sr^{2+} -UPRM-5 (TBA), confining most of the adsorption to the 8-MR pores system. Also, due to the dual pore structure of these adsorbents, tailing in the upper part of the CO_2 breakthrough curve is observed. Still, the dynamic working capacities for both Sr^{2+} -UPRM-5 variants, compare well to the equilibrium working capacities of Sr^{2+} -ETS-4 and even superior at concentrations higher than 5000 ppm. This brings out the potential of Sr^{2+} -UPRM-5 (TPA) and Sr^{2+} -UPRM-5 (TBA) for its use for gas separations in PSA systems. A quick assessment for its implementation in air revitalization systems for closed volume environments show the potential of these adsorbents for its use in larger scale setups.

Effect of continuous thermal activation between cycles showed that thermal/vacuum activation is not only unnecessary for Sr^{2+} -UPRM-5 regeneration, but also detrimental in the CO_2 adsorption working capacity. It was found that lowering the system pressure is enough to regenerate the material, as expected for any good PSA system. This represent a considerable advantage in terms of energy use efficiency proficiency for future large scale applications. Further studies regarding vacuum time for regeneration should be performed for system operation optimization.

4.7 References

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Chapter 5

Closing Remarks: General Conclusions and Future Work

The aim of this study was the synthesis and characterization of UPRM-5 using NR_4^+ cations tetrapropylammonium (TPA) and tetrabutylammonium (TBA) as SDAs and the measurements of CO_2 , N_2 and CH_4 adsorption equilibrium data, kinetic selectivity studies and fixed bed dynamic CO_2 adsorption performance using Sr^{2+} -ion exchanged UPRM-5 variants. The results are direct evidence of the potential of Sr^{2+} -UPRM-5(TPA) and Sr^{2+} -UPRM-5(TBA) for CO_2 removal from light gas mixtures.

5.1 General Conclusions

Synthesis of UPRM-5 was achieved using TPA and TBA cations as structure directing agents as confirmed by XRD. Effective detemplation with NH_4^+ and functionalization with Sr^{2+} was also completed and corroborated with FT-IR. Different levels of dehydration with activation temperature were found for each of the studied Sr^{2+} -UPRM-5 variants as shown by TGA and surface area measurements. This was related to the level of faulting, which as corroborated by ^{29}Si MAS NMR analysis is higher for Sr^{2+} -UPRM-5 (TPA). Heat of adsorption measurements showed two adsorbents with unique cation positions and loading, resulting in different surface potentials for Sr^{2+} -UPRM-5 (TPA) and Sr^{2+} -UPRM-5 (TBA). At optimal activation temperatures, Sr^{2+} -UPRM-5 (TPA) showed higher capacities at low CO_2 concentrations while Sr^{2+} -UPRM-5 (TBA) exhibited superior loadings at high CO_2 pressures. This suggest that Sr^{2+} -UPRM-5 (TPA) can be used for ultra-purification applications and Sr^{2+} -UPRM-5 (TBA) for bulk-level separations. These results also confirmed that the choice of a structure directing agent can result in adsorbents with different surface potentials and thermal contraction behavior.

Determination of the evolution with thermal treatment of the long- and local range- structural characteristics of Sr^{2+} -UPRM-5 (TPA) and Sr^{2+} -UPRM-5 (TBA) was achieved via *in situ* XRD and *in situ* NMR techniques. Indexing of the *in situ* XRD patterns showed lattice parameters corresponding to an orthorhombic structure that remained stable with adsorbent dehydration. These results also showed that thermal contraction is predominantly associated to the 8 MR pore system, explaining the differences in equilibrium adsorption capacities and diffusion rates with activation temperature. *In situ* MAS NMR demonstrated how the $\text{Si}(2\text{Si}, 2\text{Ti}_{\text{oct}})$ and $\text{Si}(3\text{Si}, 2\text{Ti}_{\text{semi-oct}})$ environments are affected with thermal treatment, being the $\text{Si}(3\text{Si}, 2\text{Ti}_{\text{semi-oct}})$ the one that exhibit higher displacement. Rehydration of the adsorbents can bring framework restoration, but with some level of atomic disorder, especially in Sr^{2+} -UPRM-5 (TPA). Kinetic adsorption measurements of CO_2 and CH_4 at ambient temperatures, showed kinetic selectivities of up to ca. 41 for Sr^{2+} -UPRM-5 (TPA) and 30 for Sr^{2+} -UPRM-5 (TBA). These results confirmed the potential of Sr^{2+} -UPRM-5 (TPA) and Sr^{2+} -UPRM-5 (TBA) for kinetic driven separations of CO_2 from natural gas effluents.

The potential of Sr^{2+} -UPRM-5 (TPA) and Sr^{2+} -UPRM-5 (TBA) for their use in PSA systems was disclosed by CO_2 dynamic adsorption measurements from CO_2/N_2 mixtures. A study of the effect of thermal regeneration between cycles of equilibrium and dynamic CO_2 adsorption, showed that thermal/vacuum reactivation between cycles is detrimental to the CO_2 adsorption working capacity, while vacuum treatment can effectively reactivate the adsorbents without further framework contraction. At a CO_2 inlet concentration of 500 ppm, Sr^{2+} -UPRM-5 (TPA) showed a higher adsorbed amount than Sr^{2+} -UPRM-5 (TBA), while at higher concentrations, Sr^{2+} -UPRM-5 (TBA) is superior. Sr^{2+} -UPRM-5 (TBA) also exhibits sharper and steepest mass transfer zones than Sr^{2+} -UPRM-5 (TPA). This behavior is attributed to the higher diffusional mass transfer

resistances present in Sr^{2+} -UPRM-5 (TPA) due to the higher amount of $\text{Si}(3\text{Si}, 2\text{Ti}_{\text{semi-oct}})$ environments relative to Sr^{2+} -UPRM-5 (TBA). Because of the dual nature of the pore structure in the Sr^{2+} -UPRM-5 framework, tailing in the upper part of the CO_2 breakthrough curves is observed. Still, the dynamic working capacities for both Sr^{2+} -UPRM-5 variants, are comparable and even superior to the equilibrium working capacities of Sr^{2+} -ETS-4. This brings out the potential of Sr^{2+} -UPRM-5 (TPA) and Sr^{2+} -UPRM-5 (TBA) for its use as tunable molecular sieve for gas separations in PSA systems.

In general, this work presents the capabilities of Sr^{2+} -UPRM-5 variants for the separation of CO_2 from gas mixtures. It also explains and describes the effective modification and improvement of these materials by the incorporation of quaternary ammonium cations, tetrapropylammonium (TPA) and tetrabutylammonium (TBA), as SDAs. This resulted in different UPRM-5 materials with unique surface characteristics as well as thermal behavior that, along with surface functionalization, can be tailored for a variety of system conditions. Moreover, the understanding, development and design of adsorbents with superior selectivity toward CO_2 places this technology a step forward in the efforts directed to find inorganic compositions that result in more cost-effective and efficient adsorption-based processes.

5.2 Future Work

The results and findings of this study allow us to make recommendations and identify further fields of study for (TPA) UPRM-5 and (TBA) UPRM-5. These are the following:

1. Modification of (TPA) UPRM-5 and (TBA) UPRM-5 can be achieved by functionalizing these materials with other divalent cations such as Ba^{2+} - and Ca^{2+} -. Thermal stability

studies and CO₂ selectivity should be performed to contrast with the Sr²⁺- functionalized variants and find the conditions in which optimum CO₂ removal performance is achieved.

2. Diffusivity parameters of Sr²⁺-UPRM-5 (TPA) and Sr²⁺-UPRM-5 (TBA) should be identified for other binary gas mixtures such as N₂/CH₄, and CO₂/CH₄ to identify its potential for kinetically driven separations. Ternary gas mixtures such as CO₂/N₂/CH₄ should be also investigated to determine the concomitant effect of these gases in the CO₂ selectivity of these adsorbents and its potential for natural gas purification. Thermal activation temperature for pore size tailoring of Sr²⁺-UPRM-5 (TPA) and Sr²⁺-UPRM-5 (TBA) should be examined to increase the selectivity of these materials towards N₂ over CH₄.
3. An activation temperature of 180°C showed to increase Sr²⁺-UPRM-5 (TPA) selectivity of CO₂ adsorption in equilibrium at low concentrations (see Chapter 3). Dynamic adsorption measurements should be performed for this material after an activation temperature of 180°C to examine how this affects CO₂ working capacities at low concentrations.
4. Regeneration studies should be done to determine the minimum effective vacuum reactivation time.
5. A PSA system design with multiple fixed beds must be assembled and tested to identify the optimum conditions and further implementation of Sr²⁺-UPRM-5 (TPA) and Sr²⁺-UPRM-5 (TBA) in this technology. PSA models may be performed to further describe the adsorbent potential for CO₂ removal in PSA systems.

Appendix A

Pure Component Adsorption Isotherms at Different Temperatures

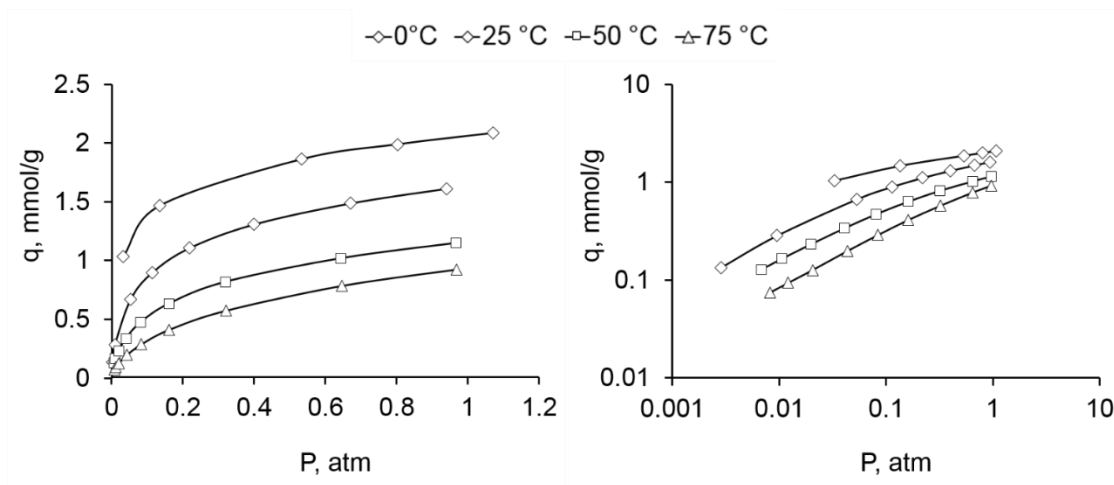


Figure A.1 Adsorption isotherms for carbon dioxide for Sr^{2+} -UPRM-5 (TPA) samples at 0, 25, 50, 75 °C. Adsorbent activated at 90 °C.

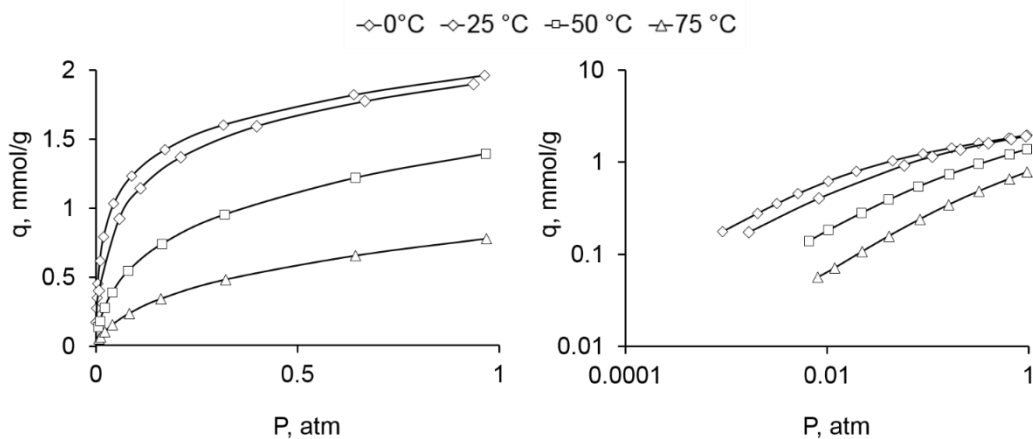


Figure A.2 Adsorption isotherms for carbon dioxide for Sr^{2+} -UPRM-5 (TBA) samples at 0, 25, 50, 75 °C. Adsorbent activated at 120 °C.

Appendix B

Crystal Length Cumulative Distributions for Sr^{2+} -UPRM-5 (TPA) and Sr^{2+} -UPRM-5 (TBA)

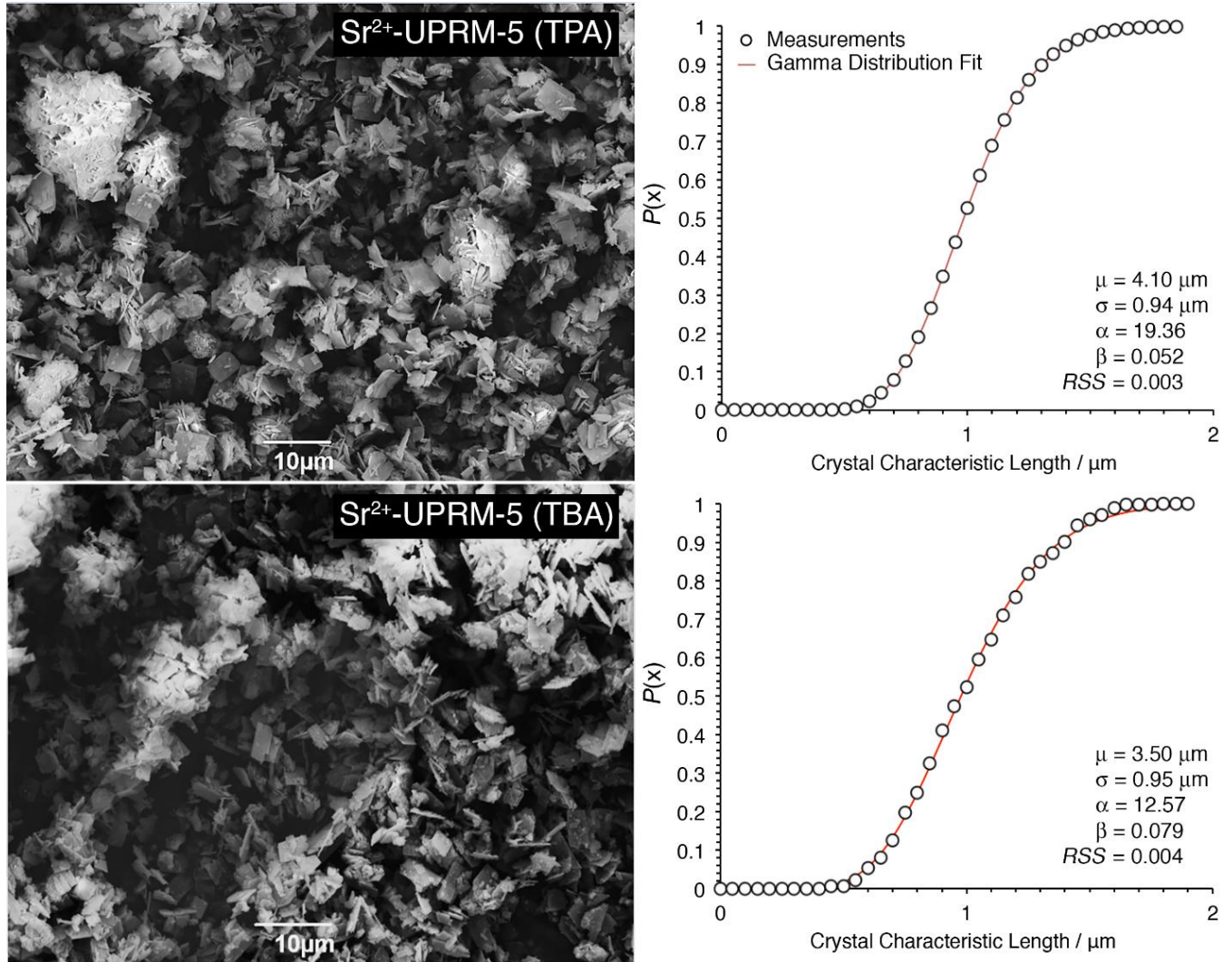


Figure B.1 SEM micrographs and corresponding crystal characteristic length cumulative distributions for Sr^{2+} -UPRM-5 prepared with different SDAs. Insets show relevant statistical parameters as well as parameters for a Gamma distribution function.

Appendix C

Volumetric Fractional Uptake including Polydispersity

```

α:=19.36
β:=.052
lave:=1.77255
a:=23.70408
b:=1.597203
d=0.037;
T=100;
c=500;
Q={0, (...), 1};
While[T<=c, d+=0.001;
  c=T;
  f[t_]:=1-NIntegrate[
$$\sum_{n=1}^{150} \left( \frac{2 * a * (1 + a)}{1 + a + a^2 * (b + \pi * (n - 1))^2} \right) \text{Exp} \left[ - (b + \pi * (n - 1))^2 * \left( \frac{d * t}{y^2} \right) \right]$$
, {y, 0, 200} ] *
1 Exp[-y/β]) / (Gamma[α] βα);
  F=Map[f,
{0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1, 1.1, 1.2, 1.3, 1.4, 1.5, 1.8, 2.4, 2.8, 3.4,
3.8, 4.4, 4.8, 5.4, 5.8, 6.4, 6.8, 7.4, 7.8, 8.4, 8.8, 9.4, 9.8, 10.4, 10.8, 11.4, 11.8, 12.4,
12.8, 13.4, 13.8, 14.4, 14.8, 15.4, 15.8, 16.4, 16.8, 17.4, 17.8, 18.4, 18.8, 19.4, 19.8, 20
.4, 20.8, 21.4, 21.8, 22.4, 22.8, 23.4, 23.8, 24.4, 24.8, 25.4, 25.8, 26.4, 26.8, 27.4, 27.8
, 28.4, 28.8, 29.4, 29.8, 30.4, 30.8, 31.4, 31.8, 32.4, 32.8, 33.4, 33.8, 34.4, 34.8, 35.4, 3
5.8, 36.4, 36.8, 37.4, 37.8, 38.4, 38.8, 39.4, 39.8, 40.4, 40.8, 41.4, 41.8, 42.4, 42.8, 43.
4, 43.8, 44.4, 44.8, 45.4, 45.8, 46.4, 46.8, 47.4, 47.8, 48.4, 48.8, 49.4, 49.8}];
  S=Take[F, {38, 113}];
  H=Take[Q, {38, 113}];
  W=S-H;
  P=W2 ;
  T=Total[P];
If[T<=c, Clear[W, P]];]
Print [T]
Print [d]
Print [F]

```

Appendix D

Unit Cell Parameters with Activation for Sr^{2+} -UPRM-5 (TPA) and Sr^{2+} -UPRM-5 (TBA)

Table D.1 Orthorhombic unit cell lattice parameters, volume, and figures of merit (FOM) for indexing as a function of material pre-activation temperature.

Adsorbent	Temperature (°C)	a (Å)	b (Å)	c (Å)	Volume (Å ³)	FOM
Sr^{2+} -UPRM-5 (TPA)	90	23.04	8.24	7.17	1361.27	175
	180	22.93	7.05	6.67	1077.21	296
	240	22.93	7.05	6.67	1077.27	144
	300	22.31	6.81	6.13	931.12	688
Sr^{2+} -UPRM-5 (TBA)	90	23.24	7.17	6.94	1157.28	98
	180	22.93	7.05	6.67	1077.16	100
	240	22.92	7.05	6.67	1077.19	100
	300	22.92	7.05	6.67	1077.19	100

Appendix E

Fractional Uptakes for Sr^{2+} -UPRM-5 (TPA) and Sr^{2+} -UPRM-5 (TBA)

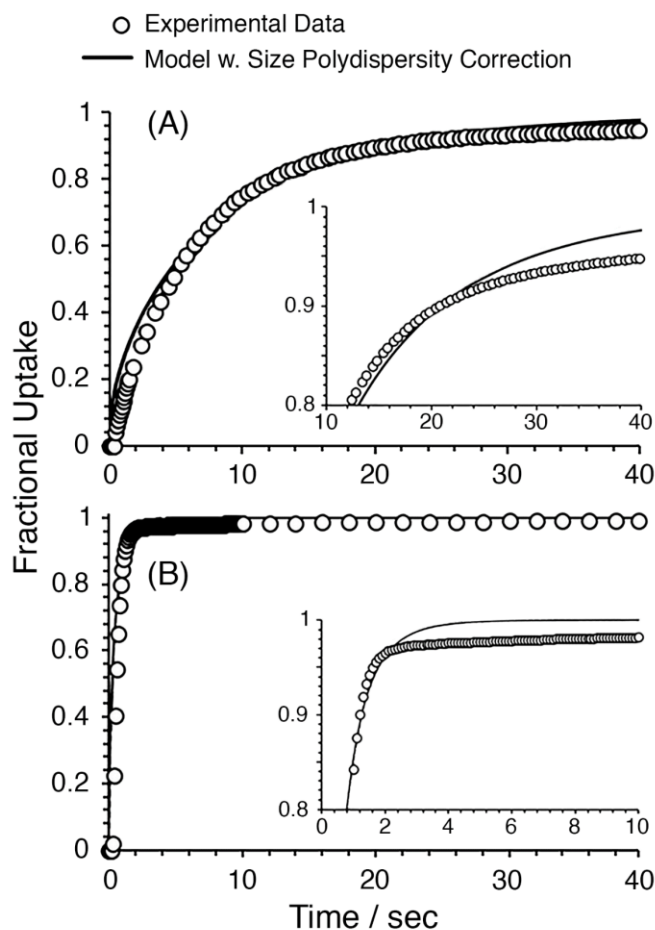


Figure E.1 Experimental CO_2 fractional uptakes and fits with volumetric transport models with and without the effect of size polydispersity for Sr^{2+} -UPRM-5 (TPA). Data obtained at a temperature of 25 °C and adsorbent activated at 90 °C. Pressure steps were (A) 0.005 atm and, (B) 0.20 atm. The graph insets show the section in the fractional uptakes for which the models have been fitted.

Appendix F

Diffusion Time Constants and Henry's Law Constant for Sr^{2+} -UPRM-5 (TPA) and Sr^{2+} -UPRM-5 (TBA)

Table F.1 Diffusion time constants for CO_2 adsorption at 25 °C, different adsorbent pre-activation temperatures, and gas pressure.

Adsorbent	Pre-activation Temperature →	90 °C			180 °C		
Sr^{2+} -UPRM-5 (TPA)	$P_{avg.}$ (atm)	$D L^{-2}$ (s ⁻¹)	ARE (%)*	RRMSE (-)**	$D L^{-2}$ (s ⁻¹)	ARE (%)*	RRMSE (-)**
	0.005	0.041	2.054	0.020	0.031	0.931	0.010
	0.05	0.080	2.118	0.024	0.133	3.736	0.044
	0.15	0.480	1.246	0.030	0.575	2.238	0.031
	0.20	0.747	1.148	0.020	0.825	1.243	0.024
Sr^{2+} -UPRM-5 (TBA)	Pre-activation Temperature →	120 °C			180 °C		
	$P_{avg.}$ (atm)	$D L^{-2}$ (s ⁻¹)	ARE (%)*	RRMSE (-)**	$D L^{-2}$ (s ⁻¹)	ARE (%)*	RRMSE (-)**
	0.005	0.040	2.148	0.024	0.042	1.223	0.014
	0.05	0.166	2.673	0.034	0.173	0.798	0.012
	0.15	0.566	1.354	0.025	0.580	1.145	0.015
	0.20	0.856	1.013	0.019	0.784	0.867	0.013

*Average Relative Error: $ARE = \frac{100}{N} \sum_{j=1}^N \text{abs} \left(\frac{F_{cal} - F_{exp}}{F_{exp}} \right)$

** Residual Root Mean Square Error (RRMSE) is given as: $RRMSE = \sqrt{\sum_{j=1}^N \left(\frac{(F_{cal} - F_{exp})_j^2}{N - M} \right)}$

Table F.2 Diffusion time constants for CH₄ adsorption at 25 °C, different adsorbent pre-activation temperatures, and gas pressure.

Adsorbent	Pre-activation Temperature →	90 °C			180 °C		
Sr ²⁺ -UPRM-5 (TPA)	$P_{avg.}$ (atm)	$D L^{-2}$ (s ⁻¹)	ARE (%)	RRMSE (-)	$D L^{-2}$ (s ⁻¹)	ARE (%)	RRMSE (-)
	0.005	0.243	0.472	0.005	0.303	0.444	0.005
	0.05	0.462	0.067	0.001	0.550	0.077	0.001
	0.15	1.186	0.180	0.006	1.284	0.063	0.001
	0.20	1.282	0.234	0.008	1.386	0.073	0.001
Sr ²⁺ -UPRM-5 (TBA)	Pre-activation Temperature →	120 °C			180 °C		
	$P_{avg.}$ (atm)	$D L^{-2}$ (s ⁻¹)	ARE (%)	RRMSE (-)	$D L^{-2}$ (s ⁻¹)	ARE (%)	RRMSE (-)
	0.005	0.184	0.886	0.012	0.154	0.678	0.009
	0.05	0.344	0.645	0.018	0.308	1.912	0.041
	0.15	0.999	0.609	0.016	0.951	0.495	0.008
	0.20	0.912	1.621	0.072	1.244	0.343	0.006

Table F.3 Henry's law constants for equilibrium adsorption at 25 °C and different adsorbent pre-activation temperatures.

Adsorbate	Sr ²⁺ -UPRM-5 (TPA)		Sr ²⁺ -UPRM-5 (TBA)	
	Act. Temperature (°C)	K_H (mmol g ⁻¹ atm ⁻¹)	Act. Temperature (°C)	K_H (mmol g ⁻¹ atm ⁻¹)
CO ₂	90	10.6	120	13.2
	180	10.0	180	9.1
CH ₄	90	0.27	120	0.31
	180	0.29	180	0.98

Appendix G

Effect of Pelletizing of Sr^{2+} -UPRM-5 (TPA) and Sr^{2+} -UPRM-5 (TBA) in the CO_2 Adsorption and Long-Range Structural Characteristics

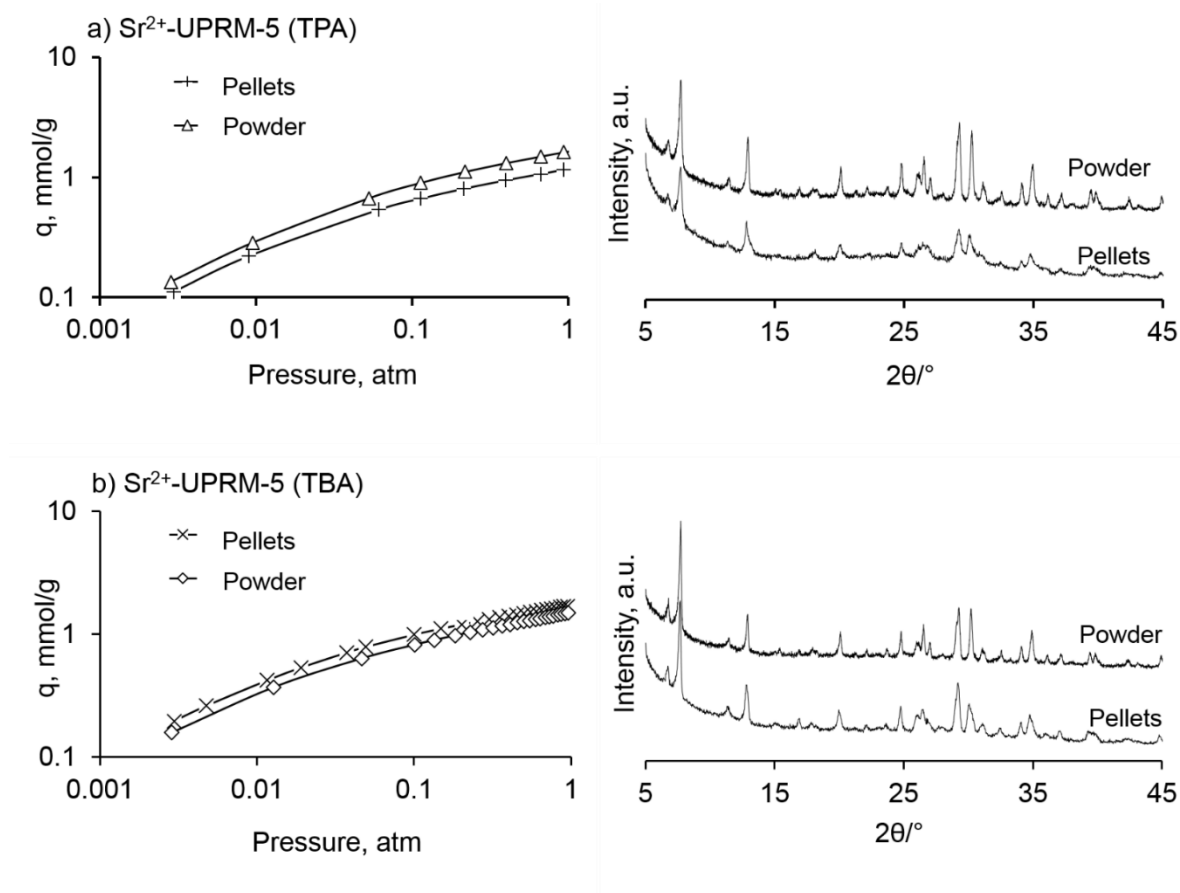


Figure G.1 CO_2 adsorption isotherms and XRD patterns for (a) Sr^{2+} -UPRM-5 (TPA) and (b) Sr^{2+} -UPRM-5 (TBA). The isotherms and the patterns were collected for both pelletized and powder materials.

Appendix H

Dynamic Adsorption Breakthrough Curves with Temperature/Vacuum Reactivation Between Cycles.

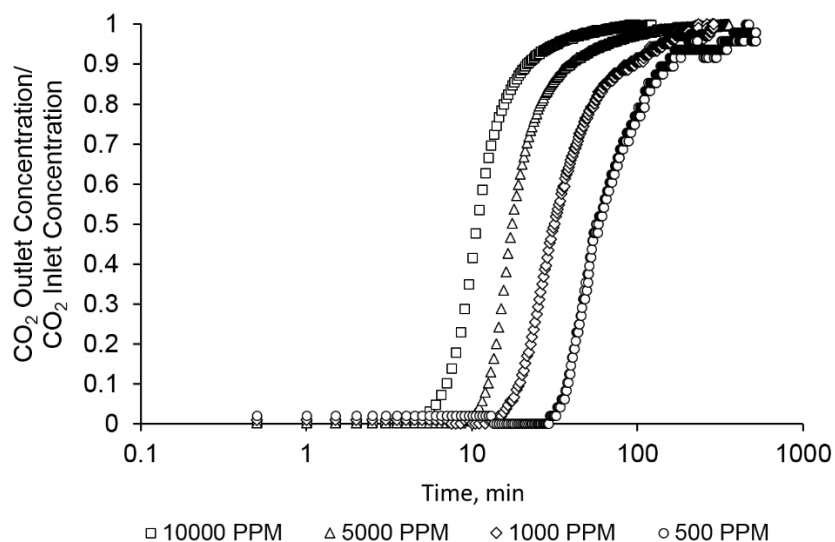


Figure H.1 CO₂ breakthrough curves in dry N₂ for feed concentrations of 10000 ppm, 5000 ppm, 1000 ppm, and 500 ppm for a Sr²⁺-UPRM-5 (TPA) adsorption bed. Thermal/vacuum treatment was performed for reactivation between cycles.

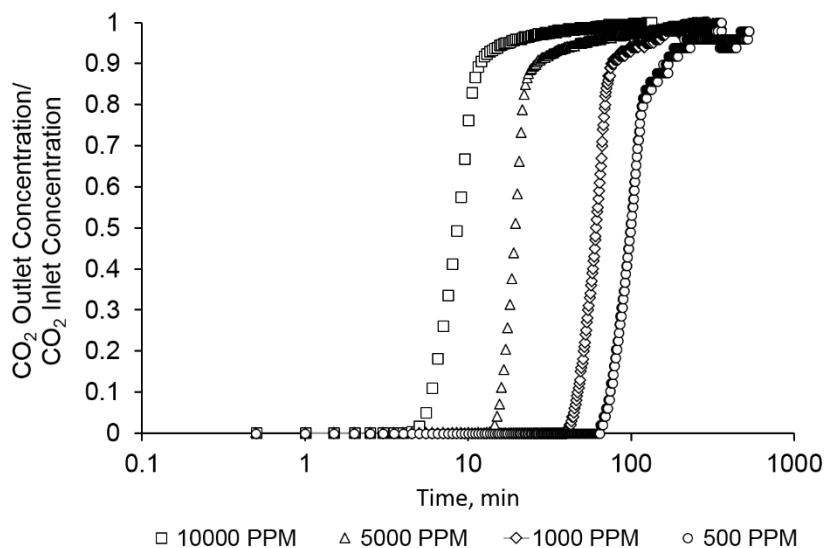


Figure H.2 CO₂ breakthrough curves in dry N₂ for feed concentrations of 10000 ppm, 5000 ppm, 1000 ppm, and 500 ppm for a Sr²⁺-UPRM-5 (TPA) adsorption bed. Thermal/vacuum treatment was performed for reactivation between cycles.

Table H.1 CO₂ dynamic and equilibrium adsorbed amounts for both Sr²⁺-UPRM-5 variants at 25°C. Thermal/vacuum treatment was performed for reactivation between cycles.

Material	C₀, ppm	Activation Temperature, °C	Time to Breakthrough (t_b), min	Amount Adsorbed at Breakthrough (q_b), mmol g⁻¹	Equilibrium Adsorbed Amount, mmol g⁻¹
Sr²⁺-UPRM-5 (TPA)	500	90	31.5	0.016	0.081
	1000	90	14	0.014	0.092
	5000	90	8.5	0.042	0.182
	10000	90	3	0.030	0.288
Sr²⁺-UPRM-5 (TBA)	500	120	67	0.032	0.096
	1000	120	41.5	0.040	0.11
	5000	120	13	0.063	0.224
	10000	120	4	0.389	0.26

Appendix I

GProms - Dynamic Adsorption Models

I.1. Sr²⁺-UPRM-5 (TPA)

1. MODEL: Adsorption Bed

PARAMETER

Bed Length, Bed Inner Diameter, Density and Cross-sectional Area

Bed_Length AS REAL

Bed_Inner_Dia AS REAL

Bed_Density AS REAL

Bed_Area AS REAL

Bed_Weight AS REAL

Bed_Volume AS REAL

Sat_q1 AS REAL

alpha AS REAL

C AS REAL

K1 AS REAL

Po AS REAL

n AS REAL

Bed and Particle Void Fraction

Bed_Void AS REAL

Particle_Void AS REAL

Particle_Density AS REAL

Rp AS REAL

Particle Tortuosity

Taup AS REAL

F AS REAL

Gas Viscosity

Viscosity AS REAL

Molecular Diffusivity

Dm AS REAL

Effective Diffusivity

De AS REAL

Diffusivity

Ds AS REAL

Molecular Weight

```

MW AS REAL
# Ideal Gas Constant
R AS REAL
# Feed Conditions
Pfeed AS REAL
Tfeed AS REAL
Yfeed AS REAL
# Volumetric Flow
Qvol AS REAL
# Superficial Gas Velocity
u AS REAL
#Axial Dispersion Coefficient
Dif_z AS REAL
DISTRIBUTION_DOMAIN
Axial AS (0 : Bed_Length)
VARIABLE
# Gas Mole Fraction
Yb AS DISTRIBUTION (Axial) OF Gas_Mole_Fraction
# Solid Phase Concentrations
qast AS DISTRIBUTION (Axial) OF Solid_Concentration
q AS DISTRIBUTION (Axial) OF Solid_Concentration
BOUNDARY
#BOUNDARY CONDITIONS FOR EQUATION 1
#z=0
Dif_z*PARTIAL(Yb(0), Axial)=-u*(Yfeed-Yb(0));#(Yb(0))=Yfeed; #
#z=Bed_Length
PARTIAL(Yb(Bed_Length), Axial) = 0.0;
#q*
FOR z := 0 TO Bed_Length DO
qast(z)=Sat_q1*(1-EXP(-alpha*((ABS(Yb(z))+Yb(z))/2+1E-8)/Po)))*EXP(-
((C*LOG(Po/((ABS(Yb(z))+Yb(z))/2+1E-8)))^n))+((ABS(Yb(z))+Yb(z))/2+1E-
8)*K1*EXP(-alpha*((ABS(Yb(z))+Yb(z))/2+1E-8)/Po));
END
#EQUATION 1
FOR z := 0 TO Bed_Length DO
$q(z)=(15*De/(Rp^2))*(qast(z)-q(z));
END
FOR z := 0|+ TO Bed_Length|- DO

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$Yb(z) = Dif_z*PARTIAL(Yb(z),Axial,Axial)-PARTIAL(Yb(z)*u,Axial)/Bed_Void-
(R*Tfeed/Pfeed)*Particle_Density*((1-Bed_Void)/Bed_Void)*$q(z);
END

```

2. PROCESS: Simulate_Adsorption

```

UNIT
Column AS Adsorption_Bed
SET
WITHIN Column DO
#BASIC INFO
Bed_Length := 0.123; # m
Bed_Inner_Dia := 0.0104; # m
Bed_Weight := 7.83E-3; # kg
Bed_Volume := 3.141592653589793*((Bed_Inner_Dia/2)^2)*Bed_Length; # m^3
Bed_Density := Bed_Weight/Bed_Volume; # kg/m^3
Bed_Area := 3.14159265358973*(Bed_Inner_Dia/2)^2; #0.0001935 (mi valor);
Bed_Void := 1-Bed_Weight/(Bed_Volume*Particle_Density);
Particle_Void := 0.44;
Particle_Density := 2013.9334;
Rp := 0.000635/2;
F := Particle_Density*((1-Bed_Void)/Bed_Void);
#*****
Ds := 0.40E-10; #m^2/s (Parameter for Iteration)
Yfeed := 0.0005; #Concentración {0.0005, 0.001, 0.005, 0.01} ;
De := (Particle_Void/Taup)*(Ds*Dm/(Ds+Dm));
Dm := 1.429E-5; # m^2/s
Dif_z := 0.7*Dm + Rp*2*u; #1.637735E-5;#0.00127516;
Taup := 3; #2.3557;
MW := [44]; # g/mol
R := 8.314; # J/mol.K
Pfeed := 1.01325E5; #(mi valor); # pa
Tfeed := 298; # K
#*****
Viscosity := 1.8E-5; # Ns/s
Qvol := 4.16667E-06; # m^3/s
u := Qvol/Bed_Area; # m/s
#PARAMETROS DE ECUACION DE q

```

```

Sat_q1 :=3.76449230287068;
n:=1.96996149309045;
alpha:=326169.905677281;
C:= 0.169852702328166;
K1:=510.567893089216;
Po:=63.18885489;
Dm := 1.429E-5; # m^2/s
Axial := [CFDM,2,200];
# Discretization Method
END # WITHIN
INITIAL
WITHIN Column DO
FOR z := 0|+ TO Bed_Length|- DO
Yb(z) = 0.0;
END
FOR z := 0 TO Bed_Length DO
q(z) = 0.0;
END
END
#Yp(0:Bed_Length,0:Rp) = 0.0;
#Y(0:Bed_Length,0:Rp) = 0.0;
#q(0:Bed_Length,0:Rp) = 0.0;
SOLUTIONPARAMETERS
OutputLevel := 0
ReportingInterval := 30
SCHEDULE
Continue for 20000;

```

I.2. Sr²⁺-UPRM-5 (TBA)

1. MODEL: Adsorption Bed

```

PARAMETER
# Bed Length, Bed Inner Diameter, Density and Cross-sectional Area
Bed_Length AS REAL
Bed_Inner_Dia AS REAL
Bed_Density AS REAL
Bed_Area AS REAL
Bed_Weight AS REAL

```

```

Bed_Volume AS REAL
Sat_q1 AS REAL
alpha AS REAL
C AS REAL
K1 AS REAL
Po AS REAL
n AS REAL
# Bed and Particle Void Fraction
Bed_Void AS REAL
Particle_Void AS REAL
Particle_Density AS REAL
Rp AS REAL
# Particle Tortuosity
Taup AS REAL
F AS REAL
# Gas Viscosity
Viscosity AS REAL
# Axial Diffusivity
Diffusivity AS REAL
# Molecular Diffusivity
Dm AS REAL
Dk AS REAL
# Effective Diffusivity
De AS REAL
# Diffusivity
Ds AS REAL
# Molecular Weight
MW AS REAL
# Ideal Gas Constant
R AS REAL
# Feed Conditions
Pfeed AS REAL
Tfeed AS REAL
Yfeed AS REAL
# Volumetric Flow
Qvol AS REAL
# Superficial Gas Velocity
u AS REAL

```

```

#Axial Dispersion Coefficient
Dif_z AS REAL
DISTRIBUTION_DOMAIN
Axial AS (0 : Bed_Length)
VARIABLE
# Gas Mole Fraction
Yb AS DISTRIBUTION (Axial) OF Gas_Mole_Fraction
# Solid Phase Concentrations
qast AS DISTRIBUTION (Axial) OF Solid_Concentration
q AS DISTRIBUTION (Axial) OF Solid_Concentration
BOUNDARY
#BOUNDARY CONDITIONS FOR EQUATION 1
#z=0
Dif_z*PARTIAL(Yb(0), Axial)=-u*(Yfeed-Yb(0));#Yb(0)= Yfeed;
#z=Bed_Length
PARTIAL(Yb(Bed_Length), Axial) = 0.0;
#q*
FOR z := 0 TO Bed_Length DO
qast(z)=Sat_q1*(1-EXP(-alpha*((ABS(Yb(z))+Yb(z))/2+1E-8)/Po))*EXP(-
((C*LOG(Po/((ABS(Yb(z))+Yb(z))/2+1E-8)))^n))+((ABS(Yb(z))+Yb(z))/2+1E-
8)*K1*EXP(-alpha*((ABS(Yb(z))+Yb(z))/2+1E-8)/Po));
$q(z)=De*(15/(Rp^2))*(qast(z)-q(z));
END
#EQUATION 1
FOR z := 0|+ TO Bed_Length|- DO
$Yb(z) = Dif_z*PARTIAL(Yb(z),Axial,Axial)-PARTIAL(Yb(z)*u,Axial)/Bed_Void-
F*(R*Tfeed/Pfeed)*$q(z);
END

```

2. PROCESS: Simulate_Adsorption

```

UNIT
Column AS Adsorption_Bed
SET
WITHIN Column DO
#BASIC INFO
Bed_Length := 0.123;

```

```

Bed_Inner_Dia := 0.0104;
Bed_Weight := 7.56E-3; # kg
Bed_Volume := 3.141592653589793*((Bed_Inner_Dia/2)^2)*Bed_Length; # m^3
Bed_Density := Bed_Weight/Bed_Volume; # kg/m^3
Bed_Area := 3.14159265358973*(Bed_Inner_Dia/2)^2; # m^2
Bed_Void := 1-Bed_Weight/(Bed_Volume*Particle_Density);
Particle_Void := 0.44;
Total_Bed_Void := Bed_Void + Particle_Void*(1 - Bed_Void);
Particle_Density := 2436.1071;
Rp := 0.000635/2;
F := Particle_Density*((1-Bed_Void)/Bed_Void);
#*****
Ds := 2E-10; #m^2/s (Parameter for Iteration)
Yfeed := 0.0005; # Concentration {0.0005, 0.001, 0.005, 0.01}
De := (Particle_Void/Taup)*(Ds*Dm/(Ds+Dm));
Dm := 1.429E-5; # m^2/s
Dif_z := 0.7*Dm + Rp^2*u;
Taup := 3; #2.3557;
MW := [44]; # g/mol
R := 8.314; # J/mol.K
Pfeed := 1.01325E5; # Pa
Tfeed := 298; # K
Rc := (3.50E-6)/2;
#*****
Viscosity := 1.8E-5; # Ns/s
Qvol := 4.16667E-06; # m^3/s
u := Qvol/Bed_Area; # m/s
#PARAMETROS DE ECUACION DE q
Sat_q1 :=3.36344;
n:=2.10266907;
alpha:=350742.5;
C:=0.164688;
K1:=259.2971;
Po:=63.18885489;
Axial := [CFDM,2,200];
Discretization Method
END # WITHIN
INITIAL

```

```

WITHIN Column DO
FOR z := 0|+ TO Bed_Length|- DO
Yb(z) = 0.0;
END
FOR z := 0 TO Bed_Length DO
q(z) = 0.0;
END
END #This end from the within
#Yp(0:Bed_Length,0:Rp) = 0.0;
#Y(0:Bed_Length,0:Rp) = 0.0;
#q(0:Bed_Length,0:Rp) = 0.0;
SOLUTIONPARAMETERS
OutputLevel := 0
ReportingInterval := 30
SCHEDULE
Continue for 20000;

```