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Nanowire based adsorbents/catalysts for CO₂ capture and utilization.

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NANOWIRE BASED ADSORBENTS/CATALYSTS FOR CO₂ CAPTURE AND
UTILIZATION.

By

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B.S., Universidad Michoacana, México, 2006

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May, 2019

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DEDICATION

This dissertation is dedicated to my beloved family and friends. Without their words of support and encouragement I could have not completed the present work.

I want to express my gratitude to my parents who, no matter the distance, were with me every step of the way making sure I stayed on track.

To my Louisville friends who helped me and stood by my side sharing those long shifts of late work, and to my friends that are far away for they always believed I could make it happen.

Finally, I want to dedicate this dissertation to the memory of my beloved ones who departed while I was away in this hard journey. I will always remember you.

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ABSTRACT

NANOWIRE BASED ADSORBENTS/CATALYSTS FOR CO₂ CAPTURE AND UTILIZATION

Apolo Nambo

April 25, 2019

Even today, the major energy source is fossil fuels, which release CO₂, a greenhouse gas that contributes to global warming. CO₂ capture, storage (CCS) and/or utilization (CCU) technologies are two routes to mitigate this problem. Sorbents are being investigated in either temperature swing or pressure swing absorption approaches for carbon capture from flue gases. Solid sorbent based technology is a promising one but suffers from slow kinetics, low capacity and need for high temperatures. Thus, new sorbent materials that can have good CO₂ sorption capacity, recyclability are sought. Similarly, one of the utilization approaches for CO₂ is dry methane reforming reaction for hydrogen production. However, current catalysts undergo sintering and produce coking at high reaction temperatures making this reaction a challenge.

In this dissertation, nanowire based materials provide uniformity of active surfaces, great stability against

sintering and improved diffusion processes for reactions are potentially interesting for fast kinetics with carbon capture sorbents and stable catalyst supports for dry methane reforming reaction.

Lithium silicate (Li_4SiO_4) nanowires were successfully synthesized using a Solvo-PlasmaTM method. Li_4SiO_4 nanowires exhibited ultrafast CO_2 sorption kinetics and capacities closer to their theoretical value. Regeneration tests have shown cyclability but have shown stability with performance at high temperatures over longer durations. The fast kinetics is attributed to shorter time scales needed for lithium to reach surface and react with CO_2 .

Titania nanowires decorated with nickel nanoparticles are investigated for dry methane reforming reaction. Results showed almost 90% CO_2 conversion and sustained the catalytic activity under harsh reaction conditions when compared to other nickel supported on spherical titania nanoparticles. The data indicates that the catalysts supported on nanowires exhibited formation of carbons that are reversibly etched in the process making them stable over long periods of time.

Overall, in this dissertation, the use of nanowire morphology is investigated to enhance CO_2 capture kinetics for improved sorption processes, and to design coke resistant

catalyst materials for dry methane reforming by boosting and modifying metal-support interactions.

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CHAPTER 1 INTRODUCTION

Around 85% of world's energy supply comes from fossil fuels¹. It is mainly the combustion of fossil fuels such as coal, oil and natural gas that supports the energy demands of our society². The CO₂ and other effluent greenhouse gases (GHGs) thus released pose enormous environmental challenges, such as global warming¹. Therefore, the separation, recovery and storage/utilization of CO₂ has been drawing tremendous attention in recent years³. CO₂ can be removed from flue gas and waste gas streams by various methods, such as membrane separation, absorption with solvents, and adsorption⁴. These technologies would help in the transition from the current use of fossil fuels to more clean energy sources in the future⁵. In the next sections, the motivations and potential of the present work are established. This chapter finalizes by outlining the research on this dissertation.

1.1 CO₂ adsorption

From all the existing technologies, the adsorption based on chemisorption processes are the best available for post-combustion. Chemisorption based adsorption involves the

interaction of CO₂ with a solid surface and reaction. The performance of chemisorption based adsorption is satisfactory at low CO₂ concentrations such as the ones found in flue gas. Chemisorption based adsorbents can deal with large amounts of dust and impurities such as SO_x and NO_x.

CO₂ capture into solid sorbents has been receiving a lot of attention since they can be used in a wide range of temperatures with less waste generated during recycling unlike liquid sorbents. Moreover their disposal requires minimal environmental protection precautions⁶. Some of the materials of interest include zeolites, porous polymers, ion exchange resins, nanofibrillated cellulose, metal organic frameworks, hydrotalcites, amines, polymeric membranes, metal oxides and different lithium ceramics^{7,8}. In recent years, different lithium ceramics have been tested as possible CO₂ adsorbents⁹. In fact, two of the most important properties of this kind of ceramics are:

- CO₂ chemisorption can be performed in a wide range of temperatures up to 650-710 °C ³
- Several of these ceramic materials are recyclable¹⁰.

Of all lithium ceramics, lithium silicates and zirconates have been extensively investigated as CO₂ sorbents.¹¹ From

these two ceramic systems the silicates have shown higher and faster CO₂ uptake. In literature the Li₄SiO₄ preparation has been found to be critical in determining its structure, composition, performance and use in potential applications.¹² Nonetheless all available lithium orthosilicate materials still suffer from slow kinetics and lower CO₂ sorption capacities than the theoretical value which affect their wide implementation in CO₂ capture systems.

1.2 Dry methane reforming

One of the most promising ways to transform CO₂ is the use of the DMR reaction. During this reaction, two major greenhouse gasses are combined to produce syngas. Syngas is considered a building block that can be used as reactants for other applications such as Fischer-Tropsch oil, methanol, and other valuable liquid fuels and chemicals¹³. This technology allows the mitigation of the most important environmental issue nowadays and provides a new generation of fuels¹⁴. The industrial application of this technology has been limited due to the lack of an effective catalyst¹⁵. One of the challenges associated with an optimum catalytic performance, is that the dry methane reforming is a highly endothermic reaction and needs to be performed at temperatures above

700°C, which is energy intensive and raises operational costs¹⁶. But the main challenges for dry methane reforming catalysts are stability, activity and coke formation.¹⁵ Therefore, an efficient, economic and stable catalyst during reaction conditions will be crucial in the industrial implementation of dry methane reforming¹⁶. A suitable catalyst for reforming will catalyze the reaction at low temperatures, will be resistant to coke formation, and will be tolerant to different concentrations of poisons (e.g. sulfur, halogens, heavy metals, etc.) for an extended period of time¹⁷.

Figure 1.1. Syngas main applications.

1.3 Nanowire based materials

Nanowires are single crystal structures with diameters below 100 nm and are several microns in length¹⁸. Nanowire materials offer two important features: shorter length scales with

diameters for reacting species and crystalline facets with uniform surface sites. The present dissertation aims to implement nanowire materials for efficient CO₂ sorption with fast kinetics and investigate coke resistant catalyst based in nanowire morphologies.

CO₂ sorption on nanowire morphologies for lithium silicate and related materials is believed to enhance the sorption kinetics and capacities. The smaller diameters allow for faster diffusion of lithium or other alkali elements from bulk to surface and higher availability of surfaces for faster reaction kinetics. Nanowire morphology has proven to reduce sintering effects at high temperatures compared to spherical morphologies for materials.

From the catalyst material perspective, the use of nanowire has been implemented to favor certain reaction pathways and enhancing the selectivity towards the desire product. This is evident in the reactions that are known as structure sensitive reactions. Supports with nanowire morphology could enhance the product distribution; this feature of nanowire-based catalyst is very interesting and it is explored in the current work.

Furthermore, nanowire morphology in carbon utilization technologies are attractive catalyst supports for improving

coke resistance of active catalyst metals and/or materials systems. Typically, nickel provides highly active sites but suffer from fast deactivation¹⁹ from carbon deposition during dry methane reforming. In the present dissertation the effect of nanowire morphology as support is introduced to CO₂ capture and utilization. Catalytically active Ni is supported on nanowires and enhances the pathway in which the CO₂ reacts with carbon deposits to form CO and clean the Ni surface.

Figure 1.2. a) Morphology enhanced decoking process in the metal active sites b) Reverse Boudouard reaction.

As shown in Figure 1.2, high availability of adsorbed CO₂ on the nanowire surface can interact with carbon deposits on Ni catalyst clusters via reverse Boudouard reaction, and remove the carbon deposit into carbon monoxide. Typically, high carbon species mobility on nickel surface leads to carbon precipitation at the hidden metal-support interface, thereby

enhancing the interactions between adsorbed CO₂ on nanowires with the deposited carbon on nickel clusters.

1.4 Objectives

The overall goal for the dissertation is to develop and understand the potential use of nanowire based materials for carbon capture and design of coke resistant catalysts formulations. The specific objectives for the dissertation include the following:

- Synthesize alkali compound nanowires using various oxidation techniques including Solvo-Plasma™ oxidation.
- Understand the kinetics and capacity of CO₂ sorption using nanowire based materials compared to spherical morphology materials.
- Analyze and validate coking resistance through morphology enhanced catalysts. Test the stability of nanowire based catalyst in the DMR reaction.
- Explore the interactions between a nanowire support and metal nanoparticles.
- Understand the steps involved in coke resistance mechanisms over nanowire materials.

This research is focused on the understanding the CO₂ adsorption-desorption mechanisms and the active metal-nanowire support interactions for the CO₂ utilization in the DMR reaction. The work here developed is a collaborative research project between the University of Louisville and Advanced Energy Materials, LLC.

The adsorption-desorption enhanced mechanisms will allow the development of CO₂ capture and utilization technologies with great impact in flue gas treatment, and also for recovering or removing CO₂ from low concentration systems (<1%). The nanowire based materials with improved CO₂ capture could be applied in the presence of low CO₂ concentrations in enclosed spaces like submarines or space capsules. Furthermore, the role of nanowire based catalysts in the utilization of CO₂ during the dry methane reaction will provide insight on the coking resistant mechanisms, these concepts could be used in other catalysis applications. An effective catalyst for the dry methane reforming reaction will boost the implementation of this promising technology and reduce the CO₂ emissions during hydrogen and fuel production all over the world. The use of CO₂ sorption materials could also be helpful for improving the efficiency of other reactions where CO₂ is a potential bi-product or product.

1.5 Organization of this dissertation

This dissertation is divided into 7 chapters. Chapter 1 introduces nanowire based materials in the CO₂ capture and utilization technologies, the potential of the nanowire based sorbents, and the challenges in the CO₂ transformation in the dry methane reforming and the scope of this research.

Chapter 2 includes current technologies of carbon capture, the challenges of solid CO₂ sorbents and reports of promising ceramics as sorbents. In this chapter the previous work of nanowire based catalysts is presented, as well as structure sensitive reactions where nanowire application can be central. Similarly, the dry methane reforming reaction mechanistic is discussed, as well as catalysts used for it. The challenges of the current research and potential solutions are layout within chapter 2.

In chapter 3 the synthesis of the materials here studied is discussed. The methodology and characterization techniques for the present work are explained. The CO₂ capture system and reactors used are described in this chapter. The catalytic testing methodology for the dry methane reforming and the furfural hydrogenolysis is presented.

Chapter 4 discusses the use of Solvo-PlasmaTM technique for the synthesis of lithium orthosilicate with different morphologies. Results of CO₂ dynamic adsorption and isotherms of adsorption are presented and analyzed.

Within chapter 5 the application of nanowire based catalysts for dry methane reforming is explored. It contains the synthesis and catalytic testing of potassium titanate and titania nanowire supports decorated with nickel. A section about the coke characterization and quantification is included.

Chapter 6 covers the use of nanowire based catalysts for structure sensitive reactions of furfural and the characterization and catalytic testing of copper decorated nanowires. It also includes the effect of operation variables and mechanisms in which the product distribution is determined.

Finally, chapter 7 summarizes the main conclusions and future work that can be done to expand and clarified the results of this research work.

CHAPTER 2 BACKGROUND

This chapter discusses the fundamentals of current research about the carbon dioxide capture and utilization. Section 2.1 includes the state of the art technologies for carbon capture as well as the challenges, advantages, and characteristics of ideal solid adsorbents. Section 2.2 introduces the advantages, potential, and published research about nanowire based materials as catalysts. The last section focuses on dry methane reforming, the mechanisms and reactions involved in it, as well as the preferred catalysts for the reaction. It also includes the coke formation mechanism, a discussion of coke reactivity and classification and literature reports on coke formation over nickel.

2.1 CO₂ capture

CO₂ capture technologies are mainly based in membrane separation, absorption or adsorption processes. Membrane separation of CO₂ has arisen as a novel concept in which a selective membrane is used to separate CO₂ from flue gas. Membrane separation uses mechanisms such as

solution/diffusion, adsorption/diffusion, molecular sieve and ionic transport depending on the material and porosity of the membrane. For CO₂ separation processes the membrane utilization has derived two main types of technologies: the gas separation membranes and the gas adsorption membranes. The Gas separation membranes use a preferential permeation mechanism through the pores to separate the CO₂ from a high pressure to a lower pressure gas stream. The differences in partial pressure and the solubility or diffusivity of CO₂ in the membrane are the key aspects of this separation. The gas absorption membranes systems use a micro porous solid membrane between a CO₂ gas rich stream and a liquid stream that absorbs CO₂. This process is a combination of membrane separation and solvent absorption technologies giving a higher removal rate by the combination of mechanisms²⁰.

Membrane separations are continuous and low cost processes with great flexibility for CO₂ concentrations above 20%. The application of membrane technology in the flue gas treatment is limited due to the low CO₂ concentration and high temperature profile of gas stream. A CO₂ concentration lower than 20% decreases the CO₂ recovery and some membranes require cooling as a pretreatment for the rich CO₂ gas stream. A low CO₂ concentration yields to low efficiency and purity of the

recovered product, which imposes the use of several units or recycling. Moreover membranes are sensitive to sulfur and other compounds²⁰.

Absorption technology is the most widely spread CO₂ capture process since it was developed over 60 years ago. Absorption technology is based on a scrubber and a stripper where the solvent (generally an amine-based solution) is cycled between the two units capturing between 85 and 90% of the CO₂²¹. The rich CO₂ gas stream (flue gas) is bubbled from the bottom of the scrubber and the solvent or solution captures the CO₂, the outlet liquid stream that is rich in CO₂ is then fed into the stripper, where CO₂ is desorbed and recovered in to a rich CO₂ stream through heating. The regenerated solvent is then cycled back to the bubbler and the cycle starts again. Many solvents and mixtures have been investigated for CO₂ absorption applications since it is the technology that has been readily available and required little modification of the current industrial facilities for its application. Amino solvents like monoethanolamine, diethanolamine, N- methyl-2-pyrrolidone, 2-amino-2-methyl-1-propanol and Piperazine have been used alone or in a mixture for CO₂ capture. Aqueous systems that have been used as an alternative to amino solvents are potassium carbonate (K₂CO₃) systems promoted with

inorganic salts (arsenates, borates, silicates and vanadates), or organics like amines and their derivatives, alkaline amino acids (arginine) and biological enzymes (carbonic anhydrase). Another option that is rising as a feasible substitute for amino compounds is the use of ionic liquids that are functionalized with aminoacid functional groups²¹⁻²³. One of the major concerns with solvent absorption implementation is the energy required for the regeneration of the solvent. With high energy requirements the thermal stability of the solvent needs to be taking into account since it can be prone to decomposition or oxidation. Another technical problem when this technology is used, is the equipment, since the majority of the solvents or solutions are corrosive or can generate corrosive components upon degradation²³.

Solid sorbents for reversible CO₂ adsorption are easier to handle and they have lower energy requirements for regeneration, higher CO₂ uptake and selectivity. The adsorption-desorption process can be done through changes in the pressure or temperature, which in the case of solid sorbents results in lower energy consumption due to the lack of large quantities of solvent and the lower heat capacities of solids²⁴.

According to Samanta et al. there are certain criteria that a material needs to satisfy in order to be considered a good CO₂ solid adsorbent. Such criteria involve CO₂ capacity, selectivity, kinetics, stability, regeneration, mechanical strength, and cost. The adsorption capacity determines how much material will be used for a determined CO₂ load and consequently the sizing of the equipment required²⁴. There are two types of capacities to be considered, the well know equilibrium capacity and the working capacity. The working capacity is defined as the CO₂ uptake in a short period of time, and industrial applications require a value higher than 3 mmol/g of adsorbent in order to compete with the well stablished solvent based systems²⁵. High selectivity towards CO₂ adsorption is desired since any other species that participate in the adsorption-desorption process, will end up as an impurity in the CO₂ affecting transportation and storage and possibly the final usage of this recovered CO₂. The adsorption-desorption kinetics have a major impact in the operational implications of cycle time and amount of material. Faster kinetics produce sharp breakout curves and result in less material for a certain CO₂ load. The overall kinetics are determined by the intrinsic reaction kinetics and the mass transfer or diffusional resistance of the gas phase through the sorbent. Solid CO₂ adsorbents need to be

stable in oxidizing atmospheres like the one present in flue gas, specially towards SO_x, NO_x and heavy metals that are usual contaminants in this effluent. Regeneration of the adsorbent should be done through several cycles of adsorption-desorption without a decline in the CO₂ capacity and with low energy requirements for the regeneration. The energy requirements for the regeneration are determined by the heat of adsorption, in the case of physisorption, it is in the range of -25 to -50 KJ/mol, while chemisorption has values between -60 to -90 KJ/mol. The ideal solid sorbent must possess the adequate mechanical strength to withstand operation conditions such a high flue gas flow, vibrations and standard handling in a wide range of temperatures. If the solid sorbent is too weak and its structure is compromised during operation, the process will need make up materials; besides, an unstable microstructure and morphology can vary the CO₂ uptake during adsorption-desorption cycles²⁴. The solid sorbent cost should be considered when industrial implementation is planned, Tarka et al considered a price of \$5/kg for a very favorable techno economic scenario and a cost of \$15/kg for non-economic scenario placing \$10/kg as the baseline cost for a CO₂ solid sorbent²⁶.

Chemisorption based solid adsorbents are the best available technologies for postcombustion CO₂ capture since their performance is satisfactory at low CO₂ concentrations, such as the ones found in flue gas, and they can deal with large amount of dust and impurities such as SO_x and NO_x. The postcombustion CO₂ capture requires solid sorbents designed for high temperature CO₂ capture such as alkali ceramics. When compared to CaO or hydrotalcite like materials, the alkali ceramics possess larger CO₂ adsorption capacities. Alkali ceramics containing lithium have a great thermal stability through cycling, and a wide range of operational temperatures at a reasonable cost²⁷.

Figure 2.1. Schematic representation of CO₂ chemisorption-desorption on Li₄SiO₄²⁸

There are several studies on Li_4SiO_4 and Li_2ZrO_3 and their performance as CO_2 adsorbents. Within these publications, it is reported that Li_4SiO_4 adsorbs more than 50% by weight relative to Li_2ZrO_3 , and does so at rates 30 times faster^{29,30}. Additionally Li_4SiO_4 is lighter and cheaper than Li_2ZrO_3 ²⁷. CO_2 chemisorption on Li_4SiO_4 takes place according to the schematic on figure 2.1.

Several CO_2 capacities have been reported for Li_4SiO_4 , with a wide range of analysis conditions. For example, one study reported an uptake of 30.3 wt.% after 95 min at 620°C with 100 ml/min flow of $\text{CO}_2:\text{N}_2$ 1:1³, while another found an uptake of 16.3 wt.% after 160 min at 560°C in 150 ml/min flow of pure CO_2 .¹⁰ The Li_4SiO_4 preparation has been found to be critical in determining its structure, composition, performance, and use in potential applications¹².

The traditional synthesis of Li_4SiO_4 is made through solid-state route that usually requires temperatures above 800 C. The high temperature synthesis results in agglomeration or sintering that produces bigger particles, smaller surface area, and poor purity^{28, 31}. Other synthetic routes for Li_4SiO_4 include sol-gel³² and precipitation³³. In the present

dissertation, a novel technique called Solvo-PlasmaTM is explored for the synthesis of 1-D structures of Li_4SiO_4 .

2.2 Nanowire based catalysts

Many industrial catalysts display a link between their catalytic performance and their metal-support interactions that depend on the nature and structure of the support. These support properties affect the active metals by modifying their size and chemical states³⁴. In recent years nanowire based catalysts have drawn a lot of attention due to their single crystal nature and faceting that improves the properties of supported catalytically-active metals. Moreover, nanowires have well-defined surface facets that create uniform active sites and nanowires morphologies are more resistant to sintering than conventional catalyst³⁵.

Since the surfaces obtained in nanowires are homogeneous, the metal-support interactions are replicated throughout the material. These dominant exposed surface facets can lead to a higher catalytic activity³⁶ or higher selectivity³⁷.

Undeniably, the interaction between reactants and specific active sites play a central role in heterogeneous catalysis. The different shapes in which a solid catalyst can be fabricated create different types of active sites, usually

located at edges, corners, and high-energy surfaces³⁸. The morphology effect has been reported as an important variable capable of open up new ways to enhance catalytic performance. La_2O_3 nanorods showed higher activity and selectivity towards oxidative coupling of methane reaction at low temperature when compared to nanoparticles³⁹. In the CO oxidation reaction CeO_2 nanorods with 110 and 100 facets were found to be more catalytically reactive than CeO_2 nanocubes with 100 facets and CeO_2 octahedrons with 111 facets³⁶. For Ir catalysts supported on nanorods, an improvement of activity, selectivity and stability in several glycerol reforming reactions was reported demonstrating the effect of morphological control in high-temperature reactions³⁸.

These findings point out to ways of enhancing catalytic performance by means of specific surface reactivity. The morphology control in nanocatalysts suggests that the catalytic activity is controlled not only by the chemical composition and size of the catalyst, but also by the type of surface sites available at the catalyst surface⁴⁰. Surface reactivity depends greatly on the density of atoms and the number of unsaturated bonds on the surface⁴¹. However, the practical application of morphology enhanced catalysts is

hindered by a number of issues, like their structural stability of nanomaterials³⁸ and facile industrial production.

In this regard, nanowire based catalysts offer an excellent opportunity to explore these advantages since new technologies are being successfully developed for industrial production of nanowires. Nanowire structures present larger aspect ratio and a higher amount of external surface sites, also they withstand reaction conditions and reduce sintering. Reports in literature about studies conducted on nanowire catalysts have increased. In the ethylene epoxidation reaction there is a great effect of selectivity depending on the nature of the dominant Ag surface facet, Ag nanowire facets provide different reaction pathways⁴². In the o-xylene combustion Cu-Ni nanowires possess numerous 100 crystal faces that promote catalytic activity⁴³. CeO₂ nanowires exhibit a larger portion of 110 and 100 and catalytically improved the activity in CO oxidation³⁶. A long-term catalytic evaluation has been performed for the CO oxidation reaction with Ni₅TiO₇ nanowires obtaining favorable results and establishing the superior stability of nanowire based catalysts⁴⁴.

Surface processes involved in heterogeneous catalysis can be improved by enhancing the accessibility of reactants to catalytic site, favoring molecular diffusion and mass

transfer. Nanowires can provide these features while tuning the surface structure and atomic arrangement of the catalyst with the exposed crystal planes⁴⁵. Furthermore, the use of metal oxide nanowire as support to disperse metal nanoparticles creates some special tailoring features of catalytic activity. Metal oxide materials are catalytically active, and in combination with metal nanoparticles offer a synergistic effect. Also, there is a strong metal-support interaction that further modifies the metal nanoparticles performance⁴⁶.

Indeed, the metal-support interactions play a major role in the overall performance of a catalytic material, and such metal-support interactions are pretty evident when structure sensitive reactions are evaluated. The structural sensitive reactions are reactions in which the reaction kinetics are influenced by the morphology of the metal particles⁴⁷. One key platform molecule in the biomass conversion is the furfural, which has been receiving major attention in the past few years and its reactions have proven to be structural-sensitive reactions⁴⁸.

Figure 2.2. Conversions of furfural to various value-added chemicals and biofuels⁴⁹

The commercial catalyst for 2 methyl furan production contains chromium or noble metals^{50, 51}. Such formulations are highly toxic or expensive and their product distribution has low selectivity towards 2 methyl furan as can be seen in table 2.1.

Table 2-1 Literature reported furfural conversion and 2methylfuran yield using different catalysts and solvents⁵²

Catalyst	Solvent	Conversion (%)	Selectivity (%)
5% Pt/C	H ₂ O	100	5
	n-Butanol	99.3	40.5
	n-Butanol-H ₂ O	99.7	30.8
	n-Decanol	94.5	23.2
	Tetrahydrofuran	99.4	0
1.4% Pt/C	H ₂ O	99.6	7.1
1.4% Pt-1.4% Ru/C	H ₂ O	100	1
1% Pt/Al ₂ O ₃	H ₂ O	97.7	0
1% Pt/MgO	H ₂ O	97.9	0.3
cis-[Ru(6,6'-Cl ₂ bpy) ₂ (OH) ₂ (CF ₃ SO ₃) ₂]	Ethanol	100	25
Cu-Cr	Octane	99.7	10.8
Cu-Fe	Octane	100	51
5% Pd/Fe ₂ O ₃	2-Propanol	87	10
5% Ru/C	2-Propanol	95	61

Current research is focus on developing catalysts that eliminate the highly toxic chromium component. Different transition metals that are important hydrogenating agents show a wide range of characteristic performances for furfural transformations; Copper tends to form furfuryl alcohol, while Palladium goes towards furan. Nickel and Platinum change from one to the other depending on the reaction conditions⁴⁷

Other early transition metals such as Cobalt, Ruthenium, Manganese, etc., are suitable for the hydrogenolysis of furfural since they can break the C-O bond⁵³.

ZnO is widely used in industrial fields thanks to its high stability, excellent performance, and low cost. Moreover, its properties rely largely on morphology, which is why ZnO has been synthesized and studied in a large number of morphologies like particles, rods, belts, tetrapods, spheres, flowers, needles, flowers, and tubular whiskers⁵⁴. ZnO nanowire supported copper and copper alloys were selected to be used in the sensitive reactions of furfural in order to elucidate the metal-support interactions on nanowire based catalysts

2.3 Dry methane reforming

As it was previously mentioned, the dry methane reforming reaction has a great potential to tackle the greenhouse gas problem since it uses and transforms CO₂ and methane which are the two most important greenhouse gasses. Carbon dioxide increase is mainly due to the burning of fossil fuels such as oil, coal, and natural gas; cement fabrication is another important anthropogenic source of CO₂. Annually, 7 gigatons of CO₂ are released into the atmosphere surpassing by far the rate of carbon capture mechanisms found in nature and leading to an accumulation of this gas over the years since 1959. Although methane is present at a lower concentration than CO₂, it has a global warming potential 21 times greater⁵⁵. The

aforementioned gasses are submitted to high temperatures to activate the molecules and rupture the C-H and C-O bonds which are very stable⁵⁶. The high energy requirements for bond breakage makes dry methane reforming a very high endothermic reaction. In this reactive environment a series of reactions can occur. Nikoo et al. presented the following table with the reactions involved in the Dry methane reforming⁵⁷.

Table 2-2 Reactions in dry methane reforming⁵⁷

Reaction	$\Delta H_{298.15}(\text{KJ/mol})$
$\text{CH}_4 + \text{CO}_2 \rightleftharpoons 2\text{CO} + 2\text{H}_2$	247
$\text{H}_2 + \text{CO}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}$	41
$2\text{CH}_4 + \text{CO}_2 \rightleftharpoons \text{C}_2\text{H}_6 + \text{CO} + \text{H}_2\text{O}$	106
$2\text{CH}_4 + 2\text{CO}_2 \rightleftharpoons \text{C}_2\text{H}_4 + 2\text{CO} + 2\text{H}_2\text{O}$	284
$\text{C}_2\text{H}_6 \rightleftharpoons \text{C}_2\text{H}_4 + 2\text{H}_2$	136
$\text{CO} + 2\text{H}_2 \rightleftharpoons \text{CH}_3\text{OH}$	-90.6
$3\text{H}_2 + \text{CO}_2 \rightleftharpoons \text{CH}_3\text{OH} + \text{H}_2\text{O}$	-49.1
$\text{CH}_4 \rightleftharpoons \text{C} + 2\text{H}_2$	74.9
$2\text{CO} \rightleftharpoons \text{C} + \text{CO}_2$	-172.4
$2\text{H}_2 + \text{CO}_2 \rightleftharpoons \text{C} + 2\text{H}_2\text{O}$	-90
$\text{CO} + \text{H}_2 \rightleftharpoons \text{C} + \text{H}_2\text{O}$	-131.3
$2\text{CH}_3\text{OH} \rightleftharpoons \text{CH}_3\text{OCH}_3 + \text{H}_2\text{O}$	-37
$\text{CH}_3\text{OCH}_3 + \text{CO}_2 \rightleftharpoons 3\text{CO} + 3\text{H}_2$	258.4
$\text{CH}_3\text{OCH}_3 + 3\text{H}_2\text{O} \rightleftharpoons 2\text{CO}_2 + 6\text{H}_2$	136
$\text{CH}_3\text{OCH}_3 + \text{H}_2\text{O} \rightleftharpoons 2\text{CO} + 4\text{H}_2$	204.8
$4\text{H}_2 + \text{CO}_2 \rightleftharpoons \text{CH}_4 + 2\text{H}_2\text{O}$	-165
$\text{CO} + 3\text{H}_2 \rightleftharpoons \text{CH}_4 + \text{H}_2\text{O}$	206.2

The main reaction can be described in 4 steps, 2 dissociative adsorption of the reagents, hydrogen spillover, and

oxidation-desorption of intermediates. The dissociative adsorption of methane is observed as the rate-limiting step of the dry methane reforming and it depends on the catalyst surface. The dissociation of methane and its dissociation products occurs in a dual site mechanism where CH_3 remains on top of the metal atom. The subsequent dissociation occurs in the same fashion but the resultant CH_2 migrates between two metal atoms in what is called bridged adsorption. The dissociative adsorption of CO_2 occurs in more varied pathways, 3 different adsorption pathways dominate this step. One possible way is when the carbon coordinates with the metallic surface while the oxygens stayed uncoordinated. There are other 2 adsorption mechanisms that involve oxygen coordination with the surface and are believed to favor dry methane reforming. The dual oxygen atoms coordination with the metal surface and the dual adsorption of carbon and one of the oxygens to the surface that leaves the remaining oxygen exposed. The CO_2 adsorption is a fast process that occurs at the interface between the active metal and the support. Hydrogen spillover can occur once the hydrogen has been dissociated from methane and related structures and migrates towards the support, which in most cases is a metal oxide. Hydrogen can generate hydroxyl groups on the support surface. The final step is the oxidation-desorption of intermediates,

and authors differ about the nature of this step. While some authors state that the oxidation of CH_x species to CH_xO is the intermediate that decompose to CO and hydrogen, some others describe that the adsorbed CO_2 reacts with the C residue left behind after continuous hydrogen dissociation from methane. In all cases the general agreement is that the formation or decomposition of the final species dictate the oxidation-desorption rate since the desorption of CO and hydrogen are fast processes⁵⁸.

Figure 2.3 Schematic representation of the reaction steps involved in dry methane reforming⁵⁹.

All these steps involve C interaction with the metal active sites, and at the high temperature required for the reaction, it could lead to coke formation, one of the major problems in which current research is focused. Carbon deposits can result in pyrolytic coke, whiskers, and gum. Gum is a carbon form that is usually found at low temperatures when a CH_x layer or

layers of graphene encapsulate a catalytic particle⁶⁰. The pyrolytic coke occurs typically above 600°C and is mainly observed when higher hydrocarbons are exposed to such high temperatures. It can be inferred that this type of carbon is the result of sudden dehydrogenation leading to a polymeric cluster of carbon residue⁶¹. The principal carbon deposit that is formed during dry methane reforming is whisker carbon also known as filamentous carbon. Whisker carbon is formed at high temperatures and is believed to be formed through the Boudouard reaction, consecutive methane dissociation and other decomposition reactions. The carbon that is formed over the metallic surface migrates towards the unexposed facet of the metallic nanoparticle and precipitates forming a strong whisker that grows until it separates the metallic nanoparticle from the support. Whisker carbon can grow to such extent that it can cause catalyst pellet breakage, increase pressure drop, cause reactor blockage and hot spots that can lead to reactor failure⁶⁰.

Since the formation regime of C deposits varies according to operation conditions and the material used as catalyst, a more standard classification of coke is made through reducibility variations according to temperature program reduction analysis. Carbonaceous residues that are easily

reduced are believed to help in a decoking process that leads to CO formation, this surface carbide is denominated α -C and displays reduction temperatures between 300 and 310°C. β -C is reduced in the range of 580 to 600 C and is attributed to amorphous carbon, which contributes to deactivation mechanisms⁶². Any carbonaceous residue that is reducible at higher temperatures is attributed to very stable graphitized carbon that participates in deactivation mechanisms and is classified as γ -C^{60, 63}.

The dry methane reforming reaction has been reported to be performed successfully by transition metals from groups 8, 9 and 10, but most of the reported research currently focuses on nickel-based systems, since Ni is much cheaper and more available⁶⁴. The table 2-3 shows some literature on Ni based catalysts reported for dry methane reforming. Ni based catalysts are active in the dry methane reforming but are very susceptible to deactivation by sintering and carbon deposition. The sintering of nickel leads to a loss of dispersion and deactivation. Ni based catalysts are active in the dry methane reforming but are very susceptible to deactivation by sintering and carbon deposition.

Table 2-3 Selected literature on Ni based catalyst for dry methane reforming

%Ni	Support	Temp. (C)	Time (hrs)	%conversion		Gas (CH ₄ /CO ₂ /x)	Ref.
				CO ₂	CH ₄		
10	Al ₂ O ₃	700	30	71	66	1/1/2	65
4	Al ₂ O ₃	750	24	86	78	1/3/14	66
3.9	MCM-41	750	30	–	69	1/1/2	67
15	Al ₂ O ₃ - 5CaO	600	3	22	13.5	1/1/3	68
6.8 mol	Al ₂ O ₃ -MgO	750	28	69.6	58	1/1/1	69
10	TiO ₂	750	24	–	50	1/1/0	70
5	BaTiO ₃	750	1	80.5	79.3	1/1/0	71
40	CeO ₂	1000	14	–	68	1/1/0	72
4.94	Zeolite BEA	700	7.5	81	38.6	1/1/0	73
15	CeZrO ₂	800	40	76	76	1/1/3	74
4.5	SiO ₂	750	11	60	47	1/1/0	75
10	ZnLaAlO ₄	700	30	36	29	1/1/3	76
5	ZSM	800	20	73	65	1/1/8	77

The sintering of nickel leads to a loss of dispersion and deactivation. Moreover, the bigger particles generated through this process are capable of generating carbon layers above 80 atoms in diameter, which are stable and remain on metal particles covering the active sites⁷⁸ and can lead to the formation of β -C or γ -C. Zhang et al studied the effect of support on carbon deposits over nickel during dry methane reforming. The following table contains their findings using 8% Ni loading, a ratio CO₂/CH₄ of 1 and 750°C⁷⁹.

Table 2-4 Effect of support on carbon deposition

Support	Carbon deposition (mg/g _{cat} h)
SiO ₂	3.0
TiO ₂	24.7
Al ₂ O ₃	16.3
ZrO ₂	21.0
MgO	4.2

In order to solve this problems Ni based catalysts research has been focusing in the use of promoters (Ce, La, Zr, Co, Mo, etc). Promoters increase the metal-support interactions avoiding sintering and inhibiting coke formation reactions⁶⁴. Authors have attributed such properties to a dilution effect of promoters that results in higher metal dispersion and smaller particle size. These promoters enhance the reducibility and resistance to oxidation. Additionally, promoters can induce changes in the reaction pathways avoiding coke formation¹⁶.

Transition metal promoters play different roles according to their nature. One of the most studied promoters is Cobalt. Cobalt promotion changes the reaction pathway since Ni-Co alloys have a strong adsorption of oxygen species, which benefits the carbon removal processes¹⁶. It has been reported

that the high coke resistance of cobalt is associated with a low activity for methane dissociation and decomposition, a good affinity for CO₂ adsorption, and a strong metal-support interactions⁸⁰. Another important promoter is Cu, but the mechanism in which copper avoids coke formation is quite different, this transition metal inhibits the dissolution of carbon in Ni, enhancing the long term stability of catalyst in dry methane reforming. It is reported that the addition of Cu to Ni forms a cage like structure on the surface of Ni, "sectioning" the surface and avoiding the formation of stable graphite nucleus⁸¹.

Current research is focused on finding a proper catalyst, especially one that is coke resistant since this is the major challenge in dry methane reforming. Coke resistant catalysts are crucial for the industrial development of dry methane reforming. Controlling particle size, nanostructure, and nature of catalyst has proven to have great effects in catalyst efficiency¹⁵. The opportunity to tune these properties through a morphology enhanced catalyst is studied in the present dissertation with the use of nanowire materials for Nickel based catalysts.

There are only limited or no studies found in literature about using nanowire enhanced properties for CO₂ capture. Similarly,

there are no prior studies on nanowire based materials for improving the coke resistance of active catalysts in dry methane reforming reaction. Even though nanowire materials are very attractive for their catalytic applications, the current nanomanufacturing technologies for the production of nanowires at large scales cannot satisfy their increasing demand⁸². Currently Advanced Energy Materials, LLC., is leading the field of nanowire production at large scale through techniques like Solvo-PlasmaTM or NanowireXTM. In sight of this leap in the scientific and industrial fields, there is a great need of a deep understanding of the properties, capabilities, and opportunities about the use of nanowire based materials as catalysts and adsorbents. Particularly in the development of CO₂ capture and utilization technologies where their applications have not been reported in the literature.

CHAPTER 3 EXPERIMENTAL METHODS AND CHARACTERIZATION TECHNIQUES

The present chapter describes the characterization techniques and experiments methodologies are described. First of all, the nanowire materials synthesis includes the description of Solvo-PlasmaTM and NanowireXTM techniques as well as catalyst preparation on nanowire supports. The characterization section has elemental descriptions on the characterization techniques employed and their functioning principles. The last three sections include the apparatus description and the methodology followed for nanowire materials testing.

3.1 Synthesis of nanowire materials

3.1.1 Lithium silicate nanowires

Three different methodologies were tested for the synthesis of one-dimensional lithium silicate materials. In a typical experiment lithium hydroxide was mixed with water and a source of silicon, milled silica powder or silicon powder, to form a paste with a molar ratio of lithium to silicon 4:1. The paste was then exposed to an oxidative treatment in one of 3

different procedures. In the thermal oxidation the paste was placed in a furnace at 650°C for two hours. When using microwave heating oxidation, the paste was exposed to microwave heating in a commercial 1kW microwave oven for 5 minutes. Lastly a novel technique called Solvo-Plasma™ (Figure 3.1) was used to prepare lithium silicate materials with different nanostructured morphologies, including nanoparticles, sheet-like structures, and nanowires. The methodology is based on a technique reported by Kumar et al using plasma oxidation with alkali salts for synthesizing one-dimensional materials with fast time scales⁸³.

Figure 3.1. A schematic illustration of various steps used in Solvo-Plasma™ synthesis.

The plasma oxidation for the Solvo-Plasma™ technique was performed using an upward atmospheric microwave plasma flame as shown in Figure 4 with power ranging from of 750 to 1200 W and for durations of around one minute.

3.1.2 Zinc oxide nanowires

ZnO nanowire supports were synthesized using the NanowireX™ technique at Advanced Energy Materials, LLC. (ADEM) The NanowireX™ technique involves the direct oxidation of molten metals into metal oxide nanowires in a microwave plasma excited gas or hydrocarbon flame.

This patented scale-up process has been developed by ADEM from bench scale to pre-commercial scale. Such process employs an upstream atmospheric plasma flame fluidized reactor, in which micron-scale metal powders are fed into the reactor. The metal powders melt and oxidize to form metal oxide nanowires. The resulting nanowire powders are collected under a cyclone and a bag house filter. This new reactor has been successfully implemented for bulk production of half a ton per day quantities of zinc oxide nanowires at its manufacturing facility.

3.1.3 Potassium titanate and titania nanowires

Potassium titanate nanowires are synthesized using an industrial scale up of the Solvo-Plasma™ technique. The powder precursors are mixed with water and the mixture is then oxidized using a patented procedure. Potassium titanate nanowire powders are obtained and then further treated to obtain titania nanowire powders.

3.1.4 Active metal decoration

All metal decorations were prepared through incipient wetness impregnation. Nitrate precursors of the metallic salts were dissolved in small amount of water. The amount of water needed was quantified according to the support to be used. In order to facilitate the dissolution of the salts the solution was heated up. The homogeneous solution was added droplet wise to the nanowire based powder and mixed thoroughly. Once the solution addition was completed, the powder was dried overnight at 120°C. Once dried the powder was calcined on a box furnace at 450°C for 4 hours. The calcined powder was collected and storage for further testing and characterization.

3.2 Materials characterization techniques

TESCAN Vega3 equipment was used to obtain scanning electron microscopy (SEM). SEM technique uses a beam of electrons focused onto the sample and scans the surface of the material. The interaction between the electron beam and the sample's surface results in the emission of electrons and photons from the sample's surface, these particles are collected by the detector and processed by the computer which generates the final image that is employed for morphology analysis⁸⁴. SEM was used to analyze the morphology of the as synthesized materials, the samples after metal decoration, and spent catalyst. Together with SEM images, information about the composition can be obtained in TESCAN SEM through energy dispersive X-ray spectroscopy (EDX or EDS), EDX allows chemical analysis of samples at the magnification level, allowing the obtention of localized compositions and elemental distribution. The coupling of these techniques uses secondary and backscattered electrons to form the images for morphological analysis and X-rays for identification and quantification of elements. EDX limits depend on the sample, the smoother the surface the lower the detection limits. In general, the EDS detection limit varies around 1%W to 10%W but for bulk materials can drop to 0.1%W⁸⁵.

X-ray diffraction (XRD) patterns were collected using a Bruker D8 Discover diffractometer with Cu K α radiation at 40 kV and 40 mA of accelerating voltage and current. XRD is a nondestructive technique that is very helpful to characterize crystalline materials since it provides information about the material structure, phases, crystal orientation, grain size, degree of crystallinity and crystal defects. The generated X-rays beam is diffracted and scattered by the lattice planes of the crystalline arrangement in the material. The resulting X-rays produce a constructive interference that is detected as a peak. Since the position and intensities are unique for a specific crystalline structure the XRD are treated as a fingerprint of the crystalline arrangement of a material.

Temperature program reduction is a powerful technique to elucidate the reducibility of a metal oxide. In this case the calcined samples are nanowire based powder with metal oxide decorations. The powder is placed between two quartz wool beds and a thermocouple is placed over it to monitor the temperature in the powder bed. The sample is degassed for 2 hours under He flow at 150°C and then cooled down. Once degassing is completed the flowing gas is changed to a mixture of 10%H₂ in Argon. The apparatus is flushed, and signal is stabilized under a flow of 50ml/min. While the signal

stabilizes, liquid nitrogen and isopropanol are mixed in a dewar under continuous stirring to prepare a cold bath. When a thick paste is formed, the dewar is placed in the cold trap. Once the signal is stable the temperature programmed reduction can begin, the furnace is heated at a constant rate and the changes in the gas composition are tracked by a thermal conductivity detector. The metal particles will be reduced according to the temperature variation. The reduction reaction consumes hydrogen and the changes in gas composition are recorded as peaks in the TPR curves.

3.3 CO₂ capture experiments

The CO₂ adsorption studies were performed using a thermogravimetric analysis (TGA) (model SDT Q600 from TA Instruments). Between 12 and 15 mg of adsorbent were placed in an alumina sample pan. Materials were degassed for 15 minutes at 150°C under 100ml/min of air flow to remove the moisture adsorbed from atmosphere. Once degassing is completed the equipment is cooled down under air flow.

Figure 3.2. Thermogravimetric analyzer SDT Q600 used for TGA data collection.

For the dynamic studies of CO_2 , adsorption samples were heat-treated dynamically from room temperature to 800°C under a gas mixture consisting of 40 ml/min N_2 (or air) and 60 ml/min CO_2 at atmospheric pressure. The isotherms of CO_2 chemisorption were tested under similar conditions, but the sample was heated to equilibrium at the desired temperature (500, 550, 600, 650 and 700°C) under 40 ml/min N_2 . Once thermal equilibrium was reached the reactive gas CO_2 was introduced in a flow of 60 ml/min. The CO_2 adsorption capacities were calculated from the adsorbent weight changes. In a recyclability analysis, a 5 cycle loop was used on the selected sample with an adsorption temperature of 700°C and

desorption stage of 720°C under a gas flow of 40 ml/min N₂ and 60 ml/min CO₂.

3.4 Dry methane reforming catalytic testing

The dry methane reforming was evaluated in a custom made packed bed reactor. A ½ inch diameter quartz tube is used as the reaction chamber. The quartz tube is placed in a vertical tubular furnace as depicted in the figure below. The gas composition is controlled by the mass flow controllers (MFC) at the inlet calibrated for He, H₂, CO₂ and CH₄.

First the catalyst is reduced in a gas flow of 20% H₂ in He at the reaction temperature for 2 hours. After this time, the gas composition is changed to a mixture of CO₂ and CH₄ and the reaction time begins, the first sampling is made at 10 minutes and subsequently every 30 minutes. Samples are taken by the sampling valve incorporated in the GC. The GC system is an Agilent 7820A with a thermal conductivity detector (TCD) and a flame ionization detector (FID) with a ShinCarbon ST micropacked column (100/120 mesh, 2m, 1/16in. OD, 1.0 mm ID). The GC analysis is done under a flow of 10 ml/min of He as carrier gas and heating program (40°C for 2 min, 10°C/min heating to 220°C and hold it for 3 min).

Figure 3.3. Diagram and picture of the custom-made packed bed reactor-GC for testing of dry methane reforming catalyst.

Once the reaction test is completed the reactor is cooled down and the catalyst is collected and stored for further analysis.

3.5 Furfural hydrogenolysis studies

The furfural hydrogenolysis testing was conducted in batch reactors. In a typical experiment, 1 gr of nanowire based catalyst powder was placed in the batch reactor for reduction with hydrogen flow at 250°C with a heating rate of 5°C/min.

After cooling down, a mixture of isopropanol and furfural was fed under nitrogen purging together with the magnetic bar for stirring.

Figure 3.4. Batch reactors property of Advanced Energy Materials, LLC. (ADEM) used in the catalytic evaluation of nanowire based catalyst for furfural hydrogenolysis.

The reactor was sealed and purged 3 times with hydrogen and then pressurized to the desired pressure. The stirring is started and the reactor is heated at 5°C/min to the desired temperature. Once reaction time is reached the reactor is cooled and the stirring system is shut down. The reaction mixture is collected and centrifuged to separate the spent catalyst that is washed with acetone and stored for further analysis.

Figure 3.5. GC-FID equipment for analysis of organic liquid samples.

The liquid reaction mixture is prepared for gas chromatography (GC) analysis. A solution of 100 μ l of liquid sample and 100 μ l of acetone is prepared and injected in a HP 6890 GC system with flame ionization detector (GC-FID). The GC analysis is performed using a split ratio 100:1 in a HP-5 (5% phenyl methyl siloxane) capillary column (30m x 320 μ m x 0.25 μ m) with 1ml/min of carrier gas flow under a temperature profile (40°C for 5 min, heating rate of 10°C/min to 220°C and held there for 7 min).

CHAPTER 4 NANOWIRE BASED ADSORBENTS FOR CO₂ CAPTURE

Anthropogenic greenhouse gasses are responsible for serious environmental challenges, most importantly global warming. CO₂ is known to be the major contributor to global warming⁸⁶. In the past decade, CO₂ capture using solid sorbents has particularly attracted immense attention from both academic and industrial fields⁶. Most lithium ceramics perform CO₂ chemisorption at elevated temperature ranges and have high recyclability^{3, 87}. The current chapter describes the fast synthesis of lithium orthosilicate nanowires through the Solvo-PlasmaTM technique. This morphology and some others are evaluated for CO₂ capture.

4.1 Lithium orthosilicate nanowire synthesis

The methodologies for the synthesis of lithium based nanowire materials described in the previous chapter for synthesis of nanowires utilized mixtures containing Li to Si about 4:1 or higher. When using plasma oxidation two different precursors of Si were used, milled silica and silicon powder (sigma-aldrich, <50 nm). Both silicon precursors were mixed in ratios

of 8:1, 6:1 and 4:1 and exposed to plasma with power of 750w for about 1 min with a flow of 10 liter/min. For the thermal oxidation experiments the mixture of LiOH and SiO₂ was placed in a box furnace at 650°C for 2 hours. The microwave heating oxidation was performed with a microwave power of 1000W for 5 minutes. Results are summarized in table 4.1 and the SEM images showing the morphology obtained are displayed in 4.1.

Table 4-1 Effect of oxidative treatment over the morphology

Oxidative treatment	Precursors	Morphology	Figure
Plasma	LiOH:SiO ₂ 8:1	Bundles of NWS	A
	LiOH:SiO ₂ 6:1	NWs	B
	LiOH:SiO ₂ 4:1	Irregular agglomerates	C
	LiOH:Si 8:1	Bundles of NWS	D
	LiOH:Si 6:1	NWs	E
	LiOH:Si 4:1	Irregular agglomerates	F
Thermal	LiOH:SiO ₂ 12:1	NWs	G
Microwave	LiOH:SiO ₂ 12:1	NWS	H

All three of the above techniques produced nanowire morphologies but the main differences are time, excess LiOH required, and resulting phases. Figure 4.2 displays the XRD of the materials synthesized with the 3 techniques.

Figure 4.1. Morphology of materials synthesized with plasma oxidation, thermal oxidation and microwave heating.

The main difference is that the plasma oxidation approach is the only one that exhibited the predominant formation of Li_4SiO_4 phase nanowires using Li to Si at molar ratios > 4 . The thermal oxidation method required Li:Si molar ratios greater than 12:1 to obtain Li_4SiO_4 phase nanowires with a duration of two hours. The microwave heating method resulted in the formation of Li_2SiO_3 . This occurred due to the presence

of water during the heating that triggered the following reaction:

Figure 4.2. SEM images and XRD of the of lithium silicate powders obtained: a) Microwave heating, b) Thermal oxidation and c) Plasma oxidation (LiOH:Si 8:1).

In all of the methods, the mixtures of lithium hydroxide and silicon precursor powders melt upon heating using thermal or microwave heating, or plasma exposure to form a molten $\text{Li}_x\text{Si}_y\text{O}_z$ phase. Subsequent oxidation of the molten phase results in the nucleation and growth of nanowires similar to our previous

work in the case of tin oxide and tinania nanowires^{83, 88}. The role of radicals and ions produced in the plasma flame play a key role in the fast nucleation and growth kinetics of the Li_4SiO_4 phase.

From these results, it is clear that the plasma oxidation results in the highest formation of Li_4SiO_4 and this methodology is followed in order to synthesize the following materials. Sample A consisted of material made using milled SiO_2 powder with a molar ratio of 4:1 and direct plasma exposure with 1200W power; sample B was synthesized using Si nanopowder and a molar ratio of 4:1 with 750W plasma power in direct plasma contact; sample C was formed by Si nanopowder, using a molar ratio of 8:1 and a plasma power of 750W with indirect plasma exposure, by placing the quartz slide containing the precursors paste with the clean side facing downwards to plasma flame directly and the side containing the paste upwards. Nanowire morphologies resulted when using over stoichiometric proportions of lithium hydroxide to silicon precursors but using careful exposure to plasma flame. After allowing the solid paste to melt with heat (1 minute), the sample is exposed indirectly to flame allowing only oxygen radicals to participate in further oxidation of the melt (30 seconds). Irrespective of plasma power, the

spherical or agglomerate morphology occurred when the samples were prepared using a stoichiometric amount of lithium hydroxide. Direct exposure to plasma lead to this type of morphology probably due to overheating. In order to prevent overheating, further oxidation reactions and sintering of nanostructures samples were prepared using an excess of lithium hydroxide and indirect exposure to plasma flame, i.e., the quartz substrate faced the plasma flame, resulting in nanowire morphology. The material was collected, washed, dried and pulverized for characterization and testing. As a control group, the commercially available Li_4SiO_4 was purchased from Fisher Scientific Company and used as received.

4.2 Characterization of synthesized materials

The Li_4SiO_4 nanoparticles and nanowires produced using the plasma oxidation method were characterized and tested for CO_2 adsorption to understand the basic relation between the nanoscale morphology and the sorption kinetics. The XRD patterns of obtained samples are shown in Figure 4.3. The pattern displayed typical reflection peaks expected for monoclinic Li_4SiO_4 phase with lattice parameters of $a=5.3 \text{ \AA}$, $b=6.1 \text{ \AA}$ and $c=5.14 \text{ \AA}$ and the space group of $P2_1/m$. In addition

to the presence of Li_4SiO_4 phase, the XRD pattern indicates the presence of unreacted precursors and the Li_2SiO_3 phase.

Figure 4.3. XRD pattern obtained from sample A, B and C. JCPDS cards: 020-0637 (Li_4SiO_4), 074-2145 (Li_2SiO_3), 027-1402 (Si), 046-1045 (SiO_2 , quartz) and 073-3444 (SiO_2).

The principal reflections with 2θ angles of 22.2, 22.6, and 33.8, ((011), (110) and (021) respectively), were monitored for all the samples prepared, using different conditions (air plasma power, time of exposure, and precursors concentration) as an indicator of yield. From the XRD

patterns, the percentage of Li_4SiO_4 present was estimated through quantitative phase analysis based on reference intensity ratios with EVA software (Bruker) and it is used to normalize the data obtained for the CO_2 adsorption, for sample C a purity of 66.4% was found with the highest amount of unreacted Si.

Surface areas of obtained samples were determined using N_2 physisorption with BET (Brunauer-Emmett-Teller) on a Micromeritics Tristar 3000 porosimeter, with a degassing temperature of 200°C for 3 hours.

Figure 4.4. N_2 physisorption isotherm of sample A.

The N_2 adsorption-desorption plot displayed a type IV isotherm, with H3 type hysteresis. The absence of limiting absorption at high P/P_0 indicates the presence of slit-shaped pores and the presence of hysteresis suggest capillary

condensation related processes.⁸⁹ The results of the BET measurements are summarized in the following Table.

Table 4-2 Morphological properties of synthesized Li_4SiO_4 .

Lithium silicate	Morphology	BET surface area	Average pore size
		(m^2/g)	(nm)
Sample A	irregular aggregates	3.44	8.84
Sample B	irregular aggregates	2.77	18.88
Sample C	nanowires	10.19	11.51
Commercial (Fisher Scientific)	spherical aggregates	6.38	18.20

SEM images of sample A (Figure 4.5(a)) showed Li_4SiO_4 agglomerates between 10 and 200 μm as a general trend. SEM analysis of sample B (Figure 4.5(b)) showed 2-20 μm particles, with irregular shape distribution ranging from ricelike to fused sheets. The observed sheet morphology is consistent with the resulting N_2 physisorption isotherm with H3 type hysteresis, suggesting capillary condensation with no limiting adsorption stage. SEM analysis of sample C (Figures 4.5(c) and 4.5(d)) indicated that it is composed of nanowire aggregates, with diameters less than 50 nm and lengths around 5 μm .

Figure 4.5. SEM images for Li_4SiO_4 samples created using plasma oxidation: a) Sample A; b) Sample B; c) and d) Sample C.

4.3 CO_2 adsorption testing results

The dynamic CO_2 adsorption tests were performed using a thermogravimetric analysis (TGA) (model SDT Q600 from TA Instruments). First, Li-silicates adsorbents (between 12-15 mg) were degassed for 15 minutes to remove the moisture adsorbed from atmosphere; and the adsorbents were placed in the alumina sample pan in TGA and heat-treated dynamically from room temperature to 800°C . The fed gas mixture consisted of 40 ml/min N_2 (or air) and 60 ml/min CO_2 at atmospheric pressure.

Figure 4.6. Dynamic CO₂ adsorption thermograms from samples A, B and C in a) nitrogen atmosphere and b) air atmosphere.

The thermograms presented in Figure 4.6 were collected in an environment containing 60 vol% CO₂ in nitrogen with a total gas flow rate of 100 ml/min at temperatures ranging from 350 to 750°C. Flow adjustments became necessary due to pressure variations during some experiments which caused the data to appear as stepwise instead of being continuous. Specifically, the stepwise behavior in experimental data in Figure 4.6 is attributed to experimental procedure used for Samples A and B. The data shown for Sample C in Figure 4.6 did not suffer from such variations with the use of a mass flow controller in the experimental setup. First and foremost, samples A and B exhibited stable thermograms at temperatures lower than 350 °C. In sharp contrast, sample C showed a partial adsorption process. From 350 to 500°C. A slight weight increase (1-3 %)

can be observed in the samples. The main CO₂ adsorption processes, however, occurred at temperatures above 500°C. All samples exhibited significant weight increases, reaching a maximum in the temperature range of 700 to 725 °C. Nevertheless, the chemisorption process for all samples occurred from 500°C under both N₂ and air environments, the maximum CO₂ adsorption temperatures were not the same under different carrier gases. For sample A, under the pure N₂ environment, the CO₂ chemisorption occurred at the temperature range of 500-650°C, and the maximum adsorption temperature was 700°C. However, under air as balance gas, the sample weight increased dramatically at 650-700°C, and the CO₂ desorption began at 725°C. For sample B using N₂ as the carrier gas, the sample weight increase rate was stable from 500 to 750°C, and it didn't reach saturation under our experimental conditions. Sample B displayed an intense weight increase at 680-700°C when air was used as carrier gas, and the CO₂ desorption process started at 725°C. As for sample C, the performance of the material under different carrier gases was very similar. The initial stage of adsorption was below 350°C, in the range of 100-300°C; contrary to samples A and B that exhibited a highly active stage after 500°C and slowly reached a maximum around 710°C. The CO₂ chemisorption seems to depend not only on temperature, but also on the type of carrier gas.

The O₂ from air seemed to benefit the carbonation process on the adsorbents at high temperatures. The CO₂ adsorption performance for the synthesized lithium silicate materials is compared to that of commercially-available Li₄SiO₄ (obtained from Fisher Scientific). The experimental results with CO₂ adsorption obtained using different lithium orthosilicate adsorbents are summarized in Table 4.3. The Li based adsorbents synthesized using the Solvo-Plasma™ technique have much better CO₂ capture performance than that of the commercial silicate in both N₂ and air environments.

Table 4-3 CO₂ uptake capacity determined from dynamic studies.

Lithium silicate	Morphology	Weight percentage from CO₂ adsorption	
		40 ml/min N₂ and 60 ml/min CO₂	40 ml/min air and 60 ml/min CO₂
Sample A	irregular aggregates	113%	129%
Sample B	irregular aggregates	114%	124%
Sample C	nanowires	128%	130%
Commercial (Fisher Scientific)	spherical aggregates	110%	118%

The CO₂ sorption capacities of the synthesized materials are further studied by measuring isotherms at different temperatures. It was observed that all of the CO₂ adsorption

isotherms exhibited exponential behavior. Moreover, higher CO₂ chemisorption capacities were observed when the samples were exposed to higher temperatures, as expected from the literature.^{90,91}

Figure 4.7. Isotherms of CO₂ adsorption on Li-silicates a) sample A, b) sample B and c) sample C at different temperatures, under 60% CO₂ in Nitrogen (100 ml/min).

As it can be seen in Figure 4.7, the thermograms from samples A and B reached the plateau behavior within 40 minutes at higher temperatures, while sample C reached this zone during

the first minutes of the experiment with a sharp weight increase in the temperature range of 600-700 °C.

In contrast to the normal smooth transition depicting increasing CO₂ capacities with temperature, an “atypical capacity-switch” was observed in all samples around 600°C, where a lower CO₂ capacity was obtained at a higher temperature, this “capacity switch” behavior had been reported in the literature⁹². In short time scales, the increase in adsorbent weight mainly depends on the CO₂ molecules adsorbed on the Li₄SiO₄ surface, whereas with long time scales, it depends on the lithium diffusion.⁹¹ Although, higher capacity and faster CO₂ chemisorption is expected for the Li-silicate adsorbents, a range of temperatures from 550 to 650°C is also associated with sintering of the Li-silicates materials that can decrease the surface area and cycle life. Thus, the capacity switch is believed to be related to the sintering phenomenon, i.e., when the sample temperature reaches the sintering point, the capacity decreases due to low surface CO₂ saturation and the CO₂ sorption kinetics are enhanced beyond this temperature resulting in higher capacities. In our results, for Sample A the capacity switch took place between equilibrium isotherm curves at 600 and 550°C at around 90 minutes. The data for Sample B (figure 4.7

b) shows that the adsorption rate (isothermal slope) was higher at 650 than 600°C during the first 20 minutes, the final capacity at 650°C was 0.076g g⁻¹ which is lower than the 0.086g g⁻¹ capacity obtained at 600°C. The behavior of Sample C was different, in the first three minutes the CO₂ capacity-switch is observed between 550°C and 650°C. The data in Figure 4.7(c) displayed CO₂ capacity increase with higher temperatures, indicating that nanowire powder sample (Sample C) does not undergo sintering unlike spherical aggregates. The data with three samples containing different morphologies in terms of particle size indicate that the capacity switch occurs earlier for smaller particles.

The nanostructured Li-silicates synthesized using Solvo-Plasma™ method exhibited higher CO₂ adsorption capacities than those obtained using conventional lithium silicates ceramics. For chemisorption, the CO₂ adsorption over the particle surface and the lithium diffusion are considered to be the rate-limiting steps of the whole CO₂ capture process. In order to study the whole adsorption processes, including the CO₂ adsorption and the lithium diffusion, all isotherms were fitted to a double-exponential model. The double-exponential equation presents as:

$$y = A\exp(-k_1x) + B\exp(-k_2x) + C \quad (1)$$

Where y represents the weight percentage of CO_2 chemisorbed; x is the time, k_1 and k_2 are the exponential parameters for the CO_2 adsorption when is kinetically controlled by chemisorption or by lithium diffusion processes respectively. A and B are constants, and C indicates the y axial intercept. Table 4-4 shows the kinetic parameters obtained from Li-silicates isotherms fitted to double-exponential model.

In order to explain the capacity and kinetic data, it is important to understand the basic mechanism involved with CO_2 sorption on Li_4SiO_4 materials. As shown in Figure 4.8, the first step involves the reaction of CO_2 with Li atoms on the surface of the sorbent creating a coating of Li_2CO_3 under a pure chemisorption controlled step. Once this layer is completely formed, new Li atoms need to diffuse throughout the carbonate layer to reach the surface and react with the chemisorbing CO_2 in a diffusion controlled stage.⁹³

In order to explain the capacity and kinetic data, it is important to understand the basic mechanism involved with CO_2 sorption on Li_4SiO_4 materials. As shown in Figure 4.8, the first step involves the reaction of CO_2 with Li atoms on the surface of the sorbent creating a coating of Li_2CO_3 under a pure chemisorption controlled step.

Figure 4.8. Schematics illustrating comparison of CO₂ adsorption mechanisms within lithium silicate materials with different morphologies.

Once this layer is completely formed, new Li atoms need to diffuse throughout the carbonate layer to reach the surface and react with the chemisorbing CO₂ in a diffusion controlled stage.⁹³

Table 4-4 Kinetic parameters obtained from Li-silicates adsorbents isotherms at different adsorption temperatures.

Sample A			
T (°C)	k ₁ (s ⁻¹)	k ₂ (s ⁻¹)	R ²
500°C	1E-03	4E-04	0.99
550°C	4E-03	4E-04	0.99
600°C	4E-03	4E-04	0.99
650°C	2E-03	4E-04	0.99
Sample B			
T (°C)	k ₁ (s ⁻¹)	k ₂ (s ⁻¹)	R ²
550°C	5E-04	5E-04	0.99
600°C	2E-03	5E-04	0.98
650°C	1E-03	5E-04	0.99
700°C	1E-03	4E-04	0.99
Sample C			
T (°C)	k ₁ (s ⁻¹)	k ₂ (s ⁻¹)	R ²
500°C	3E-03	4E-04	0.99
550°C	1E-02	4E-04	0.99
600°C	3E-02	3E-04	0.99
650°C	2E-02	6E-04	0.98
700°C	2E-02	3E-04	0.99

The samples A and B exhibited similar k_1 values while sample C exhibited an order of magnitude higher k_1 values. The isotherm data in Figure 4.7 clearly indicates that the CO₂ dramatically increased for nanowire samples within a minute confirming that the entire sorption process is controlled by the surface reaction process as shown in Figure 4.8. The k_2

values are on the same order of magnitude for all samples implying similar mechanisms on the diffusion of Li through Li_2CO_3 formed on the surface of the particle or nanowire as shown in Figure 4.8. These results are in agreement with the data from the literature,^{94, 95} for samples A and B. Sample C exhibited an order of magnitude higher k_1 values suggesting a highly active surface over the entire temperature range. Moreover, the dynamic adsorption results in Figure 4.6 show the adsorption for the lithium orthosilicate nanowires started at much lower temperatures than the typical adsorption starting temperature of 500°C.

Using the CO_2 adsorption isotherms, the activation energy in Sample C can be estimated to be close to 66 kJ/mol, slightly lower than values reported in the literature (70-105 kJ/mol).^{95, 96} It is believed that that the change in chemisorption activation energy with the morphology is due to a change in reactivity caused by a higher number of lithium atoms on the surface of the material.⁹³ The mechanistic detail shown in Figure 6 can be extended to Li_2SiO_3 nanowires. The CO_2 sorption on to Li_2SiO_3 nanowire will lead to silica core and Li_2CO_3 shell formation, which can make it difficult to be reversed upon desorption of CO_2 .

Figure 4.9. Cyclability of Lithium orthosilicate nanowires under 40 ml/min N_2 and 60 ml/min CO_2 , absorption temperature of $700^\circ C$ and desorption temperature of $720^\circ C$.

The cyclability of CO_2 sorption and desorption for nanowires sample is shown in Figure 4.9. The most drastic decrease with capacity happens during the second adsorption step, where the uptake goes from 33% for the first cycle down to 25% for the second one, and it stays approximately constant for the rest of the cycles of adsorption-desorption.

Incomplete desorption due to the limitations of the experimental setup being used are believed to be responsible for the observed decrease. In addition, the use of a low

desorption temperature may have contributed to incomplete desorption. As the nanowire powder sample was held in a pan, the sample holder shape with inaccessible regions for CO₂/carrier gas flow and the packing of the sample could have contributed to the observed decrease in subsequent cycles. Nevertheless, the data show significant reversibility with fast CO₂ sorption and desorption kinetics. Dynamic adsorption-desorption experiments using a fixed-bed or fluidized bed could mitigate the above factors.

4.4 Summary

the Li₄SiO₄ nanowires (NW) were shown to be promising for CO₂ capture with ultrafast kinetics. Specifically, the nanowire powders exhibited an uptake of 0.35 g g⁻¹ of CO₂ at an ultrafast adsorption rate of 0.22 g g⁻¹ min⁻¹ at 650–700°C. Lithium silicate (Li₄SiO₄) nanowires and nanopowders were synthesized using a Solvo-PlasmaTM technique involving plasma oxidation of silicon precursors mixed with lithium hydroxide. The kinetic parameter values (*k*) extracted from sorption and desorption kinetics obtained using nanowire powders, are one order of magnitude higher than those previously reported for the Li₄SiO₄-CO₂ reaction system. The time scales for CO₂ sorption using nanowires are approximately 3 minutes and two orders magnitude faster compared to those obtained using

lithium silicate powders with spherical morphologies and aggregates. Furthermore, Li_4SiO_4 nanowire powders showed reversibility through sorption-desorption cycles indicating their suitability for CO_2 capture applications. All of the morphologies of Li_4SiO_4 powders exhibited a double exponential behavior in the adsorption kinetics indicating two distinct time constants for kinetic and the mass transfer limited regimes.

CHAPTER 5 NANOWIRE BASED CATALYST FOR CO₂ UTILIZATION IN DRY METHANE REFORMING

The dry methane reforming reaction has a tremendous potential to help in the global warming problem by transforming CO₂, which is the greenhouse gas that contributes the most to this detrimental effect. Dry methane reforming not only uses CO₂, but also transforms the methane that has a greater global warming potential than CO₂. Moreover, with the elimination of these harmful gasses, the dry methane reforming produces syngas that can be used for synthesis of high value chemicals and fuels to satisfy the modern society energy demands. The present chapter of this dissertation is going to be focused on Ni based catalyst, since this very active metal is seen as more likely to be implemented in an industrial scale. Nickel is more available and cheaper than noble metals that have a better performance in this promising technology.

5.1 Equilibrium calculations

The first step to aboard this complex mixture of reactions is to understand its behavior in the absence of a catalyst, in

the equilibrium state. Chemkin software was used for this purpose. Chemkin software includes an equilibrium state calculation that is based on the minimization of Gibbs free energy using:

$$G = \sum_{k=1}^K \bar{g}_k N_k$$

Where:

$\bar{g}_k$ = partial molal Gibbs function

N_k = number of moles of each specie (k) in the system

K = total number of species

For ideal solutions, including gas mixtures, the partial molal Gibbs function is:

$$\bar{g}_k = g_k(T, P) + RT \ln(X_k)$$

Where:

$g_k(T, P)$ = Gibbs function of the pure species evaluated at the temperature and pressure of the system

R = universal gas constant

X_k = mole fraction of the specie k

The equilibrium solution at a certain pressure and temperature is that N_k distribution that minimizes G value in the system.

Using the equilibrium state calculation feature on Chemkin, the first equilibrium diagram to be generated is that with all the species involved in the reactions described in table 2-1.

Figure 5.1. Equilibrium distribution of species as a function of temperature at 1 Atm and equimolar feed of methane and carbon dioxide.

The diagram above shows that the major species across the temperature range from 25 to 1200°C are the ones that participate in the dry methane reforming (hydrogen, carbon

dioxide, carbon monoxide and methane) together with water and solid carbon (coke). Water and coke are the result of some undesired reactions. All these species are the smallest and simplest molecular arrangements, bigger and more complex compounds have an equilibrium molar fraction close to zero and for that reason are neglected from here on. Once the main species have been determined, a change in pressure is introduced to observe the change in the equilibrium distribution of the species along the temperature range.

Figure 5.2. Equilibrium distribution of species as a function of temperature at a) 0.5 Atm, b) 1 Atm, c) 2 Atm and d) 10 Atm.

The graphics in figure 5.2 were generated using an equimolar feed of carbon dioxide and methane with pressures of 0.5, 1, 2 and 10 Atm. For the low range temperatures, the reagent concentration (carbon dioxide and methane) increased along with the pressure producing less coke and water. In all the scenarios the carbon dioxide presents an increase in concentration in the middle range when the carbon monoxide concentration rises, this could be attributed to the disproportionation of carbon monoxide that is more likely to happen at low temperatures. Once the temperature reaches high values the disproportionation of CO ceases and carbon dioxide concentrations drop. The minimum temperature for hydrogen and carbon monoxide production was increased with the pressure. The hydrogen equilibrium composition curve remained almost the same across the pressure range, but the carbon monoxide equilibrium composition is shifted towards the hydrogen as the pressure increases. One important observation is that the temperature at which the equilibrium composition of hydrogen and coke crossed each other remains at around 625°C when pressure is below 2 Atm, it isn't until the pressure is set to 10 Atm that a small increase in such temperature is made (650°C). It is clear that a pressure change can modify the equilibrium distribution of the species, but only huge increases have a significant impact. The economic

implications of increasing the pressure system are not worth the possible benefits of such changes i.e. a ratio of hydrogen and carbon monoxide closer to 1 in a wide range of temperatures.

The next parameter that was used to understand the mechanistic of the dry methane reforming system was the ratio of methane and carbon dioxide in the feed.

Figure 5.3. Equilibrium distribution of species as a function of methane to carbon dioxide ratio a)0.5, b)1, c)2 and d)3.

As shown in figure 5.3 the ratio of methane to carbon dioxide has a great impact on the equilibrium concentration of all the species involved. Carbon dioxide and methane lines of equilibrium composition changed directly with the ratio change. The hydrogen equilibrium composition increases when the ratio of methane to carbon dioxide increases, a behavior expected since hydrogen's main source is the dissociation of methane. Coke, being the other product of the methane dissociation, increased too. Carbon that resulted from methane dissociation can remain as solid or combine with carbon dioxide to form carbon monoxide. As expected, the carbon monoxide equilibrium curves showed a decrease since the carbon dioxide decreased. As for the water equilibrium composition, it can be seen that the main impact is at elevated temperatures, where the amount of water decreased with the increase in methane to carbon dioxide ratio.

One last parameter that was analyzed utilizing the equilibrium state calculation on Chemkin software, was the presence of eluents in the feed. Figure 5.4 represents the equilibrium state distribution of species with a) pure equimolar feed of methane to carbon dioxide and b) the feed is a mixture of 5% methane, 5% carbon dioxide and 90% helium. Both scenarios used a pressure of 1 Atm and as can be seen

from the curves, both systems present almost the same distribution of species. The major differences were the curves of methane and carbon dioxide in the low temperature range, in which methane required a much lower temperature to achieve close to zero values.

Figure 5.4. Equilibrium distribution of species a) pure equimolar feed methane and carbon dioxide, b) feed consisting of 5% methane, 5% carbon dioxide and 90% of helium.

From the equilibrium state calculations, it can be perceived that the high pressure environment is not required in dry methane reforming. The desired regime to operate is at high temperature in order to obtain higher yields of hydrogen and carbon monoxide, and decrease the undesired byproducts (water and coke). The methane to carbon dioxide ratio plays a major role in product distribution and coke formation.

5.2 Potassium titanate nanowires as support for dry methane reforming

As discussed before in the present dissertation, nickel is selected since it is highly active, has lower cost than noble metals as well as higher availability. Zhang et al reported the effects of the support over carbon formation in nickel based catalyst, they found that titania has the highest carbonaceous residue formation among the most commonly used supports. For the aforementioned, titania based supports were selected in order to study the coke resistance of nanowire based materials. The first system to be studied was potassium titanates and their decoration was performed according to the methodology described in chapter 3 of this dissertation.

Figure 5.5. potassium titanate nanowires used as support for nickel.

The materials were prepared with a loading of 1% weight of nickel, calcined and reduced prior testing. Several experiments were conducted to accomplish a good operational system. For the experiments described in this section 0.2 gr of material were loaded in the reactor, a total gas flow of 100 ml/min was used under a reaction temperature of 750°C. During the first experiments after reduction, the gas flow composition was changed to an equimolar mixture of methane and carbon dioxide using argon as eluent. When collecting the chromatogram, the abundant argon peak overlapped with carbon monoxide produced during the reaction; to avoid this, the eluant gas was changed to helium to match the carrier gas used in the GC. After the carbon based components of the product mixture were identified, the sampling and running time were adjusted to program a series of injections from the sampling valve on the GC with a time spawn of 30 min. For all the experiments the automatic sampling program was started 10 minutes after the gases in the inlet were changed to the reactive mixture. As shown from the equilibrium state composition, an increase in the ratio of methane to carbon dioxide yields to higher coke formation, hence, the composition for the following experiments was set up to a ratio of 2 to promote carbonaceous deposits.

Figure 5.6. CO_2 conversion during dry methane reforming using potassium titanate as support.

In Figure 5.6 the CO_2 conversion of Ni decorated potassium titanate are shown. As it can be seen nickel over nanowire displayed a stable conversion during the 5 hours experiments when compared with commercial potassium titanate (np). The commercial decorated potassium titanate had a higher initial activity but within 3 hours, the activity dropped below the nanowire based material. Nickel and cobalt equimolar alloy showed an outstanding initial activity, but the activity gradually fell during the experiment's duration, this could be due to a partial oxidation of the cobalt since it has a

high affinity and strong oxygen-carbon bond cleavage potential.

5.3 Titania nanowires as support for dry methane reforming

Titania nanowires were obtained after the acid wash of the potassium titanate nanowires described in chapter 3. The morphology was confirmed by SEM images below, with lengths ranging from 5 μ m to 30 μ m and diameters between 100 nm up to 1 μ m. The titania nanowires were decorated in the same fashion with 1% of Ni loading, calcined and reduced for dry methane reforming testing.

Figure 5.7. Titania nanowires used as support for nickel.

When the materials were tested under the same conditions of potassium titanates their activity was almost 10 times greater, reaching carbon dioxide conversions higher than 70% across the 5 hour test. In order to evaluate the coke

deposition and the nature of the carbon deposits the materials should display an appreciable deactivation. Zhang et al. reported a high coke formation using 8% weight of nickel⁷⁹. Materials with this higher content of nickel were prepared following this report. According to the equilibrium state calculation previously discussed, the testing conditions were modified to a harsher environment to promote carbon deposits. The methane to carbon dioxide ratio was increased to 3 and the eluent was removed; a feed consisting solely of methane and carbon dioxide can increase the total amount of carbon deposits, as can be seen from figure 5.4. Also, a raise in the gas hourly space velocity (GHSV) is suggested by Jeon et al. to rapidly generate coke over dry methane reforming catalysts⁹⁷. The GHSV was changed from 30000 mlgr⁻¹hr⁻¹ to 60000 mlgr⁻¹hr⁻¹ by decreasing the amount of catalyst loaded. Under these new conditions, the nickel decorated titania based materials were tested and the data collected through a time on stream (TOS) of 30 hours are shown in figure 5.8.

Figure 5.8. CO₂ conversion during dry methane reforming using titania nanowires as support.

The Results from the catalytic testing showed a clear difference in the behavior of nanoparticles and nanowires. The carbon dioxide conversion is higher in the case of nanowire morphology reaching 89% conversion and sustain it for 30 hours. The nickel decorated titania particles had a maximum carbon dioxide conversion of 80% and decreases steadily through the entire testing time.

5.4 Coke evaluation

Titania support was selected to study coke formation since it showed very interesting results.

Firstly, the morphology of the catalyst was analyzed using SEM images. EDX analysis displayed a nickel content of 8.3 w% for commercial titania and 7 w% for titania nanowires sample.

Figure 5.9. SEM images and EDX analysis for the synthesized materials: a) commercial titania support and b) titania nanowire support.

The commercial titania support displayed particles of 500nm diameter that form agglomerates up to 50μm diameter, while nanowire support consisted in nanowires with diameters between 100 nm to 1μm and several microns in length. Both samples showed a good nickel distribution according to the mapping images (Ni showed in green). Another important morphological characteristic is the specific surface area.

Surface area obtained from nitrogen physisorption experiments are reported in the table below. Both catalyst displayed surface areas below 10 square meter per gram.

Table 5-1 Surface area of nickel decorated titania catalysts.

Catalyst	BET surface area
	(m²/g)
Ni/TiO₂ nw	2.90
Ni/TiO₂ np	5.33

XRD of both the as synthesized and the spent titania particles are displayed in figure 5.10. The titania particle samples have a TiO₂ rutile phase, in both fresh and spent catalyst. The as synthesized sample displayed nickel oxide reflections around 37 and 43 2 θ angle. In the spent catalyst the nickel has been reduced and the reflections of nickel oxide disappeared and reflections of metallic nickel (around 45 and 53 2 θ angle) appeared.

Figure 5.10. XRD of nickel decorated titania particles used as catalyst in the dry methane reforming.

There is a noticeable reflection around 26 2θ angle that corresponds with carbon graphite reflection, this reflection is broad and can accommodate reflections of other carbon formations like carbon nanotubes. In the case of nanowire morphologies, the material showed anatase phase that has low crystallinity as can be seen from the XRD in figure 5.11.

Figure 5.11. XRD of nickel decorated titania nanowires used as catalyst in the dry methane reforming.

In the spent catalyst there is a phase transformation in the support going from a low crystallinity anatase to a more crystalline anatase accompanied by rutile phase. It has been reported in the literature a similar effect in titania nanorods, a phase transformation from anatase to rutile at 750°C⁹⁸. The nickel shows a similar transition from nickel oxide to reduced nickel from the synthesized through the spent samples in both nanowires and particles. The carbon reflection at around 26° 2θ angle seemed sharper in the case of titania nanowire support, indicating a difference in

carbon deposits. From the results above, thermogravimetric analysis (TGA) was performed on the spent materials to quantify and characterize the carbon deposits formed in both supports. The TGA from the nickel decorated titania particles is reported in figure 5.12. For the analysis, a starting weight of approximately 11 mg was placed in a porcelain cup the SDT-Q600 shown in figure 3.4. The sample was heated up to 1000°C using a heating rate of 10°C per minute under 100 ml per minute of air flow. The solid line on figure 5.12 is the weight of the sample as a function of the temperature. The weight of the sample started decreasing around 508°C and stabilized in a constant weight of 9.07 mg at around 726°C. The 1.94 mg of weight loss represented 17.6% of the initial weight. This weight loss was coke being burned from the catalyst. The nominal temperature for the coke elimination was determined to be 637°C based on the derivative of the weight change (gray line).

Figure 5.12. TGA for spent nickel decorated titania particles for dry methane reforming.

The thermogravimetric analysis for the nickel decorated titania nanowires was performed in the same fashion. Figure 5.13 shows the curves obtained from the data analysis. With an initial weight of 11.13 mg, the sample started the weight lost at 486°C and finalized at around 721°C, achieving a stable the weight of 7.81mg. From the derivative of weight change curve, the nominal temperature for the coke elimination is determined to be 644°C. The weight difference was 3.32 mg, which corresponds to 29.8% of the initial weight. When comparing the carbon elimination processes of both spent

catalysts, it is evident that for the nanowire morphology the carbonaceous residues are eliminated in a lower temperature than in the case of particle titania supports.

Figure 5.13. TGA for spent nickel decorated titania nanowires for dry methane reforming.

The thermogravimetric analyses include the heat flow curves and derivate of heat flow. From the latter it can be appreciated that in the case of nickel decorated titania nanowires the carbon elimination presented 2 thermal stages, the first one is a small peak occurring around 509°C.

The nature of carbonaceous residues can be further identified by temperature programmed reduction (TPR). As discussed in the background chapter of this dissertation there are three types of carbonaceous residues in accordance with their reducibility, α -C, β -C and γ -C. For the purpose of quantifying the amount generated of each type, the spent catalysts were loaded in a U quartz tube and placed in a furnace to control the temperature profile. A mixture of hydrogen and argon was passed through the spent catalyst and the outlet gasses were analyzed using a thermal conductivity detector (TCD).

The TPR profiles are shown in figure 5.14, where it can be seen that the titania particles support have a different distribution of carbon residues than nanowire based catalyst. The TPR profiles displayed a low temperature reducible carbonaceous material(α -C) below 300°C. From 300 to 600°C it is determined to correspond to β -C reduction, and from above 600°C the very stable graphitized γ -C. For the quantification of carbon types the TPR profiles were integrated and the relative content was determined with the area ratios.

Figure 5.14. temperature program reduction of spent catalyst
a) commercial titania support b) titania nanowire support

From the analysis of the reducibility of carbon deposits the table 4.4 was generated.

Table 5-2 Distribution of carbon type residues according to their reducibility determined by TPR

Carbon type	Commercial titania support	Titania nanowire support
α -C	42.12 %	56.28 %
β -C	15.31 %	42.83%
γ -C	42.55 %	0.89%

When comparing the very stable γ -C relative content of both spent catalysts, it is clear that the elevated graphitized carbon content on titania particles played a major role in the deactivation process.

The transmission electron microscopy (TEM) images from the as synthesized and spent catalyst showed interesting details about the morphology effects on the carbon deposits.

Figure 5.15. TEM images of commercial titania support: as synthesized (a and b) and spent catalyst (c and d).

The as synthesized material showed well dispersed nickel oxide nanoparticles of around 10 nm in diameter. In the spent catalyst the nickel nanoparticles displayed an increase in diameter reaching around 50nm. It is evident that the nickel dispersed nanoparticles are sintered after the high temperatures required for the reaction (750°C).

Figure 5.16. TEM images of titania nanowire support: as synthesized (a and b) and spent catalyst (c and d).

From figure 5.16, it can be appreciated that the nickel oxide nanoparticles of the nanowire based catalyst share the same average diameter (10nm) than the commercial titania material. The spent nanowire based catalyst TEM images exhibited a metallic nickel that maintained a nanoparticle diameter of around 10nm.

The sintering effect in the different morphologies can be observed when images 5.15 d and 5.16 d are contrasted. The diameter difference resulted in a different nanomorphology of the carbon deposits. The big nickel nanoparticles of commercial titania based catalyst generated a layer of carbon around metallic nickel. It seems that once the layer is formed around the nickel particle, like in figure 5.15 d, the nickel inside migrates and the nucleation process continues. This could explain the resulting irregular carbon structures observed in figure 5.15 c that look like interconnected cages.

In contrast with the carbon formation in the nanowire based materials where the small nickel nanoparticles resulted in a more uniform distribution of the carbon layers, i.e. figure 5.16 d where the structure formed can be described as a well ordered multiwall carbon nanotube.

5.5 Summary

In this chapter the dry methane reforming reaction was performed over 2 different titania based nanowire supports. Nanowires of potassium titanate and titania were decorated using the incipient wetness impregnation. When tested for the dry methane reforming the nanowire materials achieved higher conversion and showed a stable trend in the catalytic activity when compared with their commercially available counterparts. Potassium titanate system exhibited low carbon dioxide conversions while the titania nanowire reached almost 90% of CO₂ conversion and maintained the activity through 30 hours of TOS. The Ni over titania nanowire was contrasted with a similar material using commercially available titania which displayed a decreasing activity during the testing. Coke was quantified through TGA analysis for both systems and nanowire morphology yielded almost the double content of carbon residues than titania particles. The type of carbon deposited played a major role on the catalytic deactivation, 42.55% of the coke in commercial titania catalyst was graphitized γ -C in contrast with less than 1% for the nanowire based catalyst.

CHAPTER 6 NANOWIRES AS CATALYST SUPPORTS: FURFURAL HYDROGENOLYSIS

The properties of nanowire as catalyst can be further exploited when structure sensitive reactions are used. In chapter 2 of this dissertation the structural sensitive reactions were introduced as an application where nanowire based catalyst could generate a great impact. Structural sensitive reactions of furfural are of interest since they can produce a large variety of products (figure 2.3). Among furfural derivatives the 2-methylfuran is the most promising gasoline bio-additive, it possesses a high octane number of 103, a higher thermal efficiency than gasoline and it can be used in gasoline blends without further modifications⁹⁹.

One key parameter to tune the reactivity of metallic nanoparticles is the metal support interactions. In this regard ZnO described a strong correlation between its properties and the morphology in which it is synthesized⁵⁴. In this chapter a series of catalyst based on copper were tested in the hydrogenolysis of furfural to produce 2methyl

furan and their performance is linked to the metal-support interactions.

6.1 Catalyst preparation

ZnO nanowire supports were synthesized as described in chapter 3 at Advanced Energy Materials, LLC. Figure 6.1 show the SEM images of the ZnO supports that were used to deposit copper and copper alloys through incipient wetness impregnation. The copper loading in all the catalyst was fixed to 10% weight.

Figure 6.1. ZnO nanowire supports provided by Advanced Energy Materials, LLC. (ADEM)

The copper based metallic alloys were prepared using cobalt and nickel in a 6% weight loading. Metal precursors were diluted in distilled water and added slowly while mixing with ZnO nanowire powders. The resultant materials were dried

overnight and calcined at 450°C for 4 hrs with a heating rate of 5°C/min.

The materials obtained after calcination were characterized through XRD, Nitrogen physisorption and TPR. The XRD pattern of the synthesized materials are displayed on figure 6.2, where the highly crystalline ZnO phase is present in all samples, with high intensities in Cu/ZnOnw sample.

Figure 6.2. XRD pattern of synthesized materials after calcination

As for the Cu content it is displayed for Cu/ZnOnw as CuO Tenorite while in the other two samples a segregation of Cu occurred showing the diffractions correspondent to Tenorite

and the formation of correspondent alloys with possible incorporation of Zn. The BET analysis of the nitrogen physisorption curves were used to obtain the specific surface area of the catalyst prepared, results are displayed in table 6.1.

Table 6-1 Specific surface area of catalyst prepared

Catalyst	BET Surface area ($\text{m}^2/\text{g}_{\text{cat}}$)
12%Cu-88%ZnO	8.5
12%Cu-6%Co-82%ZnO	10
12%Cu-6%Ni-82%ZnO	7

The surface area is quite similar for all materials prepared. The temperature program reduction was performed under 50 ml/min gas flow using a mixture of 10% hydrogen in argon with a heating rate of 10°C per minute. TPR profiles of the synthesized materials are shown in figure 6.3. The reducibility of the synthesized samples goes as $\text{Cu} < \text{Cu-Ni} < \text{Cu-Co}$. CuO show the highest reduction temperature. Lower reduction peaks are associated with highly dispersed CuO and mixed oxides highly dispersed in close contact with ZnO^{100} .

Figure 6.3. TPR profile of catalysts synthesized.

6.2 Catalytic test

Catalyst were tested in batch reactors showed in figure 3.4 and following the procedure described previously. Morphology enhancement for the selective hydrogenation of furfural was tested by comparison of 2 materials with the same composition using ZnO with 2 different morphologies, particle and nanowires. Commercially available ZnO was used to synthesized copper and cobalt materials with a loading of 1% weight of

copper and cobalt. Table 6.2 display the conversions of furfural for the 2 different morphologies.

Table 6-2 Conversion of furfural over different morphologies of ZnO

Catalyst	Conv (%)
1%Cu-1%Co/ZnOnw	57.7
1%Cu-1%Co/ZnOnp	40.09

Nanowire supported material reached higher conversion under identical reaction conditions indicating the superior performance of nanowire-based materials as catalyst for the furfural hydrogenation reaction.

Figure 6.4. Schematic representation of metal and metal alloy decorations over ZnO nanowire.

The furfural selective hydrogenation was performed under different conditions and the conversion and selective was monitored. The chemical environment in the liquid phase reaction have a direct impact in the product distribution. The solvent plays a major role in the occurrence of side reactions in the liquid phase. The solvent polarity modifies the solvent-reactant interactions and modifies the hydrogenolysis activity⁵². Isopropanol and cyclohexanol were used in the selective hydrogenation of furfural as solvents. The table 6-3 contain the product distribution and conversion of furfural selective hydrogenation reactions performed.

Table 6-3 Effect of solvent over the product distribution in the furfural selective hydrogenation.

Solvent	Catalyst	conv %	Selectivity%		
			Methyl furan	Furfuryl alcohol	Others
Isopropanol	Cu/ZnO nw	59.27	0	95.21	4.78
Isopropanol	Cu-Co/ZnO nw	83.34	1.4	76	22.6
cyclohexanol	Cu/ZnO nw	100	18.4	52.7	28.9
cyclohexanol	Cu-Co/ZnO nw	91.8	26.5	50	23.5
cyclohexanol	Cu-Ni/ZnO nw	100	6.6	54.4	39

Cyclohexanol achieved higher conversion and higher selectivity of methyl furan than isopropanol. In both cases the copper cobalt alloy display higher selectivity to 2 methyl

furan. The higher performance of the copper cobalt alloy can be explained by the following mechanism.

Figure 6.5. Mechanism for selective hydrogenation over bimetallic surface.

The high affinity of cobalt towards oxygen allows better adsorption of the furfural molecule by means of the carbonyl group. The longer the molecule remain adsorbed the more hydrogen atoms can be added to the molecule resulting in the formation of 2 methyl furan. When nickel it is used the hydrogenation potential of the alloy is increased and the aromatic ring is more likely to undergo hydrogenation leading to an increase of side reactions and unwanted products.

Figure 6.6. XRD of the Cu-Co decorated ZnO nanowires.

The XRD shown in figure 6.6 show the as synthesized and the spent catalyst. During the reaction the copper cobalt alloy developed into a mixed oxide, some of the oxygen atoms from the carbonyl group remain on the metallic active sites.

Another important variable that affect the adsorption-reaction-desorption system is the initial hydrogen pressure in the system. The following table contain the product distribution as a function of the initial hydrogen pressure when copper cobalt alloy over zinc oxide nanowires is used as catalyst. The results show that a lower initial pressure has a direct correlation with 2 methyl furan production. Since the 2 methyl furan is the component of the system with the

highest vapor pressure, the low pressure promotes the volatilization of the formed 2 methyl furan. The 2 methyl furan that is vaporized decreased the liquid concentration of the desired product and displace the equilibrium towards its formation.

Table 6-4 Effect of initial hydrogen pressure over the product distribution.

Initial Pressure (psi)	Selectivity%		
	2-MF	Furfuryl alcohol	Others
10	82.2	0	17.8
100	30.7	29.9	39.4
200	14.4	34.1	51.5
300	19.9	21.1	59

The results here presented were the basis for the patent 62775150 entitled "Catalyst Compositions for Conversion of Furfural to 2-Methylfuran and their Applications". Some of the results here presented are included in this patent filed by Advanced Energy Materials, LLC.

6.3 Summary

In this chapter the high dispersion, sintering resistance, strong metal support interactions, and enhanced surface interactions with reactants of nanowire-based catalyst were

used in a liquid phase reaction that is well known to be a structure sensitive reaction.

The nanowire morphology achieved higher conversion when compared to commercial ZnO. The copper cobalt alloy displayed a better performance than pure copper or copper nickel alloy and decreased the undesired products. Results showed a direct correlation with the reducibility of the active metal sites. Cobalt can promote a better interaction with the carbonyl group and enhance the performance of the catalyst. In this chapter other operational variables were evaluated in the selective hydrogenation of furfural. It was determined that solvent and hydrogen pressure have an impact on the product distribution of the selective hydrogenation of furfural.

CHAPTER 7 CONCLUSIONS AND RECOMMENDATIONS

The current dissertation aims to expand the carbon capture and utilization technologies by including the nanowire based materials in this field. For carbon capture technologies the present work presented different morphologies of lithium silicates as CO₂ solid sorbents. Lithium orthosilicate nanoparticles, sheets and nanowires were synthesized using a new type of process using plasma oxidation with reaction time scales of about a minute. These materials were used in CO₂ sorption experiments to understand their capacity and kinetics. Results suggested that all samples synthesized in this study could lead to a higher CO₂ uptake than commercially available lithium silicate (18% uptake). Subsequent analysis indicated that the lithium diffusion occurred in the same fashion according to k_2 while the distances of this process varied greatly throughout samples, reaching 25nm (radius) in the nanowire sample providing a fast lithium supply to the surface for this morphology. The sorption capacity of 25% by wt. within a time scale of just 3 minutes demonstrates that

nanowire morphology leads to an ultrafast CO₂ adsorption, radically decreasing two orders of magnitude the time scales when compared to all other morphologies and exhibited sorption capacity close to theoretical values. Moreover, the synthesis of nanowire morphologies through our plasma oxidation technique leads to a fast scalable way to obtain materials targeting systems where diffusion barriers are detrimental.

The carbon utilization technologies here studied were focused on CO₂ transformation through the dry methane reforming reaction. The present work studied the potassium titanate and titania nanowires as nickel support for the dry methane reforming. These systems were selected since the titania based materials have been reported to have the highest coke formation among the usual supports.

The potassium titanates were tested with low conversion despite the potassium reports of enhancing the dry methane reforming by accelerating the decoking mechanism^{101, 102}. Perhaps the high content of potassium in the titanates nanowires allowed potassium to migrate over the nickel nanoparticles. Adams et al. reported that potassium can cover and neutralize active nickel sites for the dry methane reforming¹⁰³. Future work with this system can include a

variation on the acid wash conditions to achieve gradients of potassium removal. A lower content of potassium could remove the negative effects and retain the coke resistant properties on the catalyst.

The titania nanowire system achieved almost 90% CO₂ conversion with a sustain stability over 30 hours of TOS. Studies revealed that the deactivation resistance was related to the carbon stability. The nanowire based catalyst had 29% of carbonaceous residues and commercial titania had only 17% but with a very different reducibility distribution. TPR analysis showed that nanowire catalyst had less than 1 % of graphitized γ -C that is only reducible above 600°C. The TEM images revealed that nickel over commercial titania suffered sintering during DMR reaction and produced bigger nickel nanoparticles (50nm) than nanowire titania (10nm). The difference in the nickel nanoparticle can be associated to the disorder level on the carbon nanotubes produced¹⁰⁴. Further studies on the control of nickel nanoparticles and the distribution of coke type in the DMR reaction are needed to clarify their correlation with the stability observed in this study.

The titania nanowire supports studied had a phase transformation over the course of the DMR reaction. A thermal

pretreatment at high temperatures before the nickel impregnation is suggested to discard any effects of the support phase change on the observed results.

The application of nanowire based materials for climate change countermeasures was further explored. 2-methyl furan is an important bio-additive for gasoline. Furan molecules reactions are structure sensitive reactions where nanowire based catalyst can improve the selectivity towards the desired products. Here we report higher conversion for nanowire based catalyst than the commercial ZnO support. Cu-Co alloys over ZnO nanowire demonstrated to have higher 2 methyl furan selectivity and decreased the undesired product formation. The performance of the materials showed some correlation with the reducibility of the metallic nanoparticles. Solvent and pressure demonstrated a major role in the performance of the Cu alloy over ZnO nanowires.

The nanowire based catalyst here presented proved to have good performance when compared to similar specific surface area materials. Future work should be focused on replicating the mechanistic over higher surface area nanowires or on the recyclability endurance of nanowire based catalyst to achieve a benchmark that compete with traditional catalysts.

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CURRICULUM VITAE

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Summary

10+ years of experience in material science, synthesis and characterization focusing in heterogeneous catalysis.

Hands on experience in operating and troubleshooting chemical reactors and analytical instrumentation. Enthusiastic team player/leader with great communication abilities, hardworking philosophy and adaptable problem-solving skills.

Skills

Material synthesis: Solvo-plasma, Solvo-thermal, modified co-precipitation, Hydrotalcites, MOF's, zeolites, metal oxide nanowires, extrudates, surface functionalization, supported metal and metal oxides catalysts.

Characterization techniques: SEM, TGA/DCS, XRD, NMR, TPO, TPR, TPD, BET, UV-IR

Chemical reaction engineering: Packed bed reactors, Batch reactors, Parr instruments, Micromeritics microreactors, custom made glass reactors, photo reactors.

Analytical: GC-TCD/FID/MS, titration (permanganometry, Iodometry, Compleximetry, Acid-Base, potentiometric, etc.), melting point, cloud point, sulfur analysis, NMR-H, photospectroscopy.

Languages: English (full command), Spanish (full command), French (60%) and German (30%).

Experience

Advanced Energy Materials [2017-Present]. Associate Research Engineer (Curricular Practical Training)

- Developed materials for applications in sponsored projects such as: "Commercialization and Production of Ultra-Deep ULSD HDS Catalysts" (Kentucky Science and Technology Corporation), "Development of Nano-Metal Oxide Catalysts to Produce Value-Added Chemicals and Fuel Additives from Xylose" (Kentucky Science and Engineering Foundation), "Novel CO₂ Sorbent Materials for Carbon Capture Technologies" (Department of Energy).
- Engineered activity testing procedures and developed analytical methodologies for products.
- Analyzed characterization and performance data of materials and formulations for industrial applications and research purposes.

SADCOM DE OCCIDENTE S.A. DE C.V. [2007-2008]. Production supervisor in evaporation and storage department.

- Responsible for evaporation and storage areas, in charge of 20+ operators and their assignments in operation and maintenance of industrial equipment.
- Formulated operation manuals for industrial equipment. Trained new and returning personal to the assigned areas.
- Organized work schedules and planned maintenance projects.

PEPSICO / GEUSA DE OCCIDENTE S.A DE C.V. [2005-2006]. Environmental, health and safety intern

- Strengthened tasks distribution and planning.
- Implemented safety and hazard prevention measurements.
- Reviewed Equipment distribution.

University of Louisville/ Universidad Michoacana de San Nicolas de Hidalgo/ Universidad Vasco de Quiroga. [2003-2016]. Teaching assistant/ Tutor/ Trainer. Through the years I have been involved in tutoring at undergraduate and below levels.

- Coached high performance student for academic competitions in chemistry Olympics.
 - Handled teaching and evaluations for students in high school, bachelor and graduate level in chemistry and related areas.
 - Guided bachelor and graduate level courses and laboratories in front of a group as teaching assistant.
- Miscellaneous: research projects, research residences, creativity projects in several academic activities involving posters, science fairs mentorships and workshops.

Educational background

PhD Candidate in Chemical Engineering, University of Louisville, Louisville, KY	[2012- 2019]
Dissertation: "Nanowire Based Adsorbents/Catalyst for CO ₂ Capture and Utilization"	
MS in Chemical Engineering Chemical Engineering Department, U.M.S.N.H., Morelia, Michoacán México	[2008-2011]
Dissertation: "Hydrotalcite Type Mixed Oxides Zn-Al-La as Catalysts"	
BS in Chemical Engineering Chemical Engineering Department, U.M.S.N.H., Morelia Michoacán México	[2001-2006]

Selected conference proceedings

- (1) Nambo, A. et al., Fast CO₂ Sorption Kinetics Using Nanowire Based Materials. ECS-2018 meeting 2018.
- (2) Nambo, A et al., Decarboxylation and Further Isomerization of Oleic Acid over Pt- Supported on Small Pore Zeolites and Hydrotalcite Catalysts. AICHE 2014 2014.
- (3) Nambo, A. et al., ZnO Nanorods As Catalyst for Biodiesel Production Via Methanolysis of Olive Oil. AICHE 2013 2013.
- (4) Nambo, A. et al., Cu₃(BTC)₂ Metal-Organic-Framework As a Solid Acid Catalyst for the Production of Biodiesel. AICHE 2013 2013.

Selected Publications

- (1) Nambo, A.; He, J.; Nguyen, T. Q.; Atla, V.; Druffel, T.; Sunkara, M., Ultrafast Carbon Dioxide Sorption Kinetics Using Lithium Silicate Nanowires. *Nano Letters* 2017, 17 (6), 3327-3333.
- (2) Song, Z.; Nambo, A.; Tate, K. L.; Bao, A.; Zhu, M.; Jasinski, J. B.; Zhou, S. J.; Meyer, H. S.; Carreon, M. A.; Li, S.; Yu, M., Nanovalved Adsorbents for CH₄ Storage. *Nano Letters* 2016, 16 (5), 3309-3313.
- (3) Akram, M. Z.; Atla, V.; Nambo, A.; Ajayi, B. P.; Jasinski, J. B.; He, J.; Gong, J. R.; Sunkara, M., Low-Temperature and Fast Kinetics for CO₂ Sorption Using Li₆WO₆ Nanowires. *Nano Letters* 2018, 18 (8), 4891-4899.
- (4) Ahmadi, M.; Nambo, A.; Jasinski, J. B.; Ratnasamy, P.; Carreon, M. A., Decarboxylation of Oleic Acid Over Pt Catalysts Supported on Small-Pore Zeolites and Hydrotalcite. *Catalysis Science & Technology* 2015, 5 (1), 380-388.
- (5) Nambo, A.; Miralda, C.; Jasinski, J.; Carreon, M., Methanolysis of Olive Oil for Biodiesel Synthesis Over ZnO Nanorods. *Reac Kinet Mech Cat* 2014, 1-13.
- (6) Xie, Z.; Zhu, M.; Nambo, A.; Jasinski, J. B.; Carreon, M. A., Microwave-assisted Synthesized SAPO-56 as a Catalyst in the Conversion of CO₂ to Cyclic Carbonates. *Dalton Transactions* 2013, 42 (19), 6732-6735.