

University of Crete

Department of Materials Science and Technology

Master Thesis:

"Porous Materials for the Catalytic Conversion of CO₂ to Cyclic

Carbonates"



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Ευχαριστίες

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Abstract

Due to climate change, global warming, and the finite supply of energy supplies, environmental challenges have garnered a lot of academic and technological attention during the past few decades. The development of novel technologies based on cuttingedge materials for CO₂ capture and conversion is necessary due to the escalating amounts of CO₂ emissions that contribute to global warming. Porous organic polymers are ideal candidates for possible uses in CO₂ collection and conversion because they have the necessary features, such as large surface areas, narrow pore size distribution, strong chemical and thermal stability, and functional groups. The synthesis of porous polymer networks based on porphyrin (TMP-net) and aluminum porphyrin (Al-TMPnet) moieties is described in this work. Tetra-methacrylate porphyrin cross-linker production was the key step in creating porous polymeric networks. In this work, First a porous porphyrin network (TMP-net) was prepared by free-radical polymerization of the tetra-methacrylate porphyrin derivative, employing azobisisobutyronitrile (AIBN) as the initiator. Next, the TMP-net was metalated by using dimethyl aluminum chloride, to create the aluminum porphyrin-based network (Al-TMP-net). Scanning electron microscopy (SEM) was used to characterize the networks' morphology after drying them in supercritical CO₂ conditions, and Attenuated Total Reflection Fouriertransform infrared (ATR-FTIR), Energy-dispersive X-ray spectroscopy(EDS), X-ray photoelectron spectroscopy (XPS), Ultra were used to confirm that the networks had successfully metallized. The BET surface area was measured by applying the Brunauer-Emmet-Teller (BET) method to the adsorption branch of the N₂ isotherms of the polymers, with TMP-net having 622 m²g⁻¹ while the Al-TMP-net showing lower BET surface area at 167 m²g⁻¹. Additionally, at 273 K, the porous TMP-net absorbed more CO₂ than the Al-TMP-net (1.54 mmol/g vs. 0.64 mmol/g, respectively). Also, both polymeric networks, TMP-net and Al-TMP-net were used as catalysts to study their catalytic performance in the presence of TBAB as co-catalyst, for the cycloaddition of CO_2 in epichlorohydrin.. Proton nuclear magnetic resonance (¹H-NMR) spectroscopy was used to ascertain the yield of the conversion of epichlorohydrin into the cyclic carbonate derivative. The results of the experiments revealed that Al-TMP-net had a high catalytic activity with a 93% conversion at 100°C, 1 atm, and 24 h of reaction time, whereas TMP-net performed similarly well with an 88% conversion during the same reaction. Finally, recycling experiments were conducted showing the stability of the catalysts after 5 runs.

1. Introduction

1.1 Porous materials

For their numerous potentials uses in catalysis, gas collection, separation, and storage, biomedicine, among other fields, porous materials have attracted a lot of attention in recent years ^{[1],[2],[3][4]}. Porous materials differ greatly from their bulk counterparts in terms of their properties, including unique optical, chemical, and electrical behavior. This is because of the pores and the vast surface area they have. Porous materials can be categorized into three groups according to the size of their pores: microporous (pore diameter Dp 2 nm), mesoporous (pore diameter Dp 50 nm), and macroporous (pore diameter Dp > 50 nm).^{[5],[6]} Additionally, porous materials can be divided into inorganic, organic, and hybrid (organic-inorganic) materials based on their structural makeup.

The zeolites are considered the most significant microporous inorganic crystalline substances. Zeolites make excellent materials for gas sorption and extremely attractive heterogeneous catalysts due to their enormous surface areas, strong ion exchange capacities, and narrow pore-size distributions.^{[7],[8]}

Due to its unique structure, organic-inorganic (hybrid) porous materials known as metal-organic frameworks (MOFs) have received a lot of attention in the field of material science. Under benign circumstances, MOFs can be created using a variety of techniques as solvothermal, ultrasonic, microwave treatment, etc. MOFs have special qualities due to their structure, including high porosity, open pores, stability against air, etc. MOFs are frequently utilized in processes including heterogeneous catalysis, photocatalysis, and gas storage and separation.^[9] However, MOFs exhibit poor electrical conductivity and low structural stability that has an impact on their practical performance.^[10]

1.2 Porous organic polymers

Porous organic polymers (POPs), which are porous substances made from organic monomers, have grown in popularity recently because of their porousness, excellent physicochemical stability, chemical activity, and high structural variety. POPs can be categorized into five groups based on their network formation ^[11]: triazine-based frameworks, conjugated microporous polymers, covalent organic frameworks, and

polymers of inherent microporosity (PIMs).^[9] Solvothermal treatment, free radical polymerization ^[12], emulsion polymerization ^[13], suspension polymerization ^[14], high internal phase emulsion ^[15], and other processes can all be used to create porous polymers.

POPs are most frequently used in gas separation processes like CO_2/N_2 and CH_4/CO_2 separation. Gas separation results from various interactions between porous materials and the gas molecules, from the ability of the material's pores to exclude molecules of various sizes, or from a combination of the aforementioned factors. POPs are also utilized as catalysts because of their design and functionalization potential.^[16]

1.3 Porphyrins and metalloporphyrins

Due to their widespread presence in natural systems and high potential for use in a variety of applications, including catalytic reactions, the conversion of solar energy, etc., porphyrins have received a lot of attention in recent years. The Greek word porphyra, which signifies purple, is where the term porphyrin gets its name. Porphyrins, as their name suggests, are deep purple in color and can either be found in nature or created artificially. They consist of an aromatic macrocycle ring, four pyrrole rings connected by four methine bridges, and these. ^[17] (Scheme 1.1)



Scheme 1.1 Structure of porphyrin

Due to their intriguing catalytic behavior in chemistry and biology, metalloporphyrins have also received a lot of attention recently. ^[18] By incorporating a metal into the porphyrin framework, new properties are obtained, enabling the application of

porphyrins in new scientific disciplines. Examples include the usage of Mn- and Gdporphyrins in MRI.^[19]

Porphyrins and metalloporphyrins can be used for a variety of purposes, including electron transfer, catalysis, gas separation and storage, optoelectronic devices, etc. ^[17]

1.4 Porous porphyrin-based networks

BET surface areas of 910 m2/gr have been achieved through the synthesis of nanoporous polymer networks based on porphyrins.^[20] Additionally, polyporphyrins have been created with surface areas as high as 1522 m2/g, and measurements of hydrogen absorption showed a small increase in the heat of adsorption following the insertion of Fe(II) ions into the porphyrin rings.^[21] In a different investigation, Sander-Maier reaction-produced porphyrin-based hyperbranched polyimides with BET surface areas up to 682 m2/gr were created.^[22] Although most porphyrin-based systems exhibit high BET surface areas, there are systems that exhibit much lower areas. As it is shown in the following work^[23], the polymer skeleton exhibited no micropores with BET surface area 9-29 m²/g.

1.5 Carbon dioxide (CO2) capture and conversion

Large volumes of CO₂ have been emitted into the atmosphere over the past few years as a result of human activities like fuel combustion in transportation. Lowering the pH of the seas is one of the effects of these high CO₂ levels, which also cause climate change. Technology has developed methods to capture CO₂ and transform it into other, more valuable molecules in order to reduce pollution. ^[24] Additionally, the production of cyclic carbonate from epoxy compounds utilizing various catalysts uses CO₂ as a significant feedstock. The creation of efficient catalysts for the conversion of epoxy compounds to cyclic carbonates is of utmost importance for practical applications because cyclic carbonate compounds have numerous industrial applications, including as aprotic solvents, precursors for the synthesis of polycarbonates, and intermediates in the synthesis of organic compounds.^[25]

1.6 Catalysis

A catalyst, according to IUPAC, is a chemical that speeds up a process without changing the overall standard Gibbs energy. ^[24] The catalyst typically alters the reaction's course and speeds it up. Each molecule can take part in numerous consecutive

cycles because the catalyst is not consumed throughout the process, necessitating the use of relatively little catalyst in comparison to the substrate. The substrate to catalyst ratio represents the catalyst's effectiveness, which is expressed as the Turnover Number (TON) or Turnover Frequency (TOF), depending on whether the time factor is considered. Catalysts come in a wide variety of forms, including proton (H+), Lewis acids, organometallic complexes, organic or inorganic polymers, and enzymes. Although the catalysts and process conditions in each category may be very varied, the principles of each type of catalyst are the same. The main advantages of catalysis include the consumption of the desired product more quickly, the use of fewer resources, and the creation of less waste because the catalyst often opens a selective channel to the desired product. There are numerous methods for choosing a product. Chemoselectivity is a state in which two different chemical reactions can occur and produce two different products. Site selectivity happens when the same chemical reaction occurs in different locations inside a molecule, producing different results. Diastereoselectivity refers to the selectivity in each of the two (or more) diastereomers produced by a reaction, whereas enantioselectivity is used specifically when the two products are enantiomers. Depending on their level of oxidation, water content, etc., catalysts can exist in a variety of states. These states can speed up processes to different degrees and with distinct physicochemical characteristics. Solid catalysts, which can significantly speed up chemical processes, are present during industrial chemical reactions. Heterogeneous catalysts have attracted a lot of attention the past years due to their high surface area which increases the interaction of various materials with the catalyst and hence improves performance and chemical and thermal stability during the catalysis. The advantage of the heterogeneous catalyst compared to homogeneous is the easier separation from the reaction mixture.^[26] Some of the most known heterogeneous catalysts are ionic liquids, organic materials, MOFs etc.

1.7 CO₂ cycloaddition reaction

The utilization of high-energy substances like epoxides to react with carbon dioxide to produce oxidized, low-energy synthetic targets is one of the most efficient methods for converting carbon dioxide. In cycloaddition reaction of CO₂ different kinds of materials are used such as ionic liquids^[27], organic-inorganic composites (SiO₂-MOFs) ^[28] and zeolites^[29].

The reaction that takes place in the cycloaddition reaction is a ring opening reaction of an epoxide resulting a cyclic carbonate ^[30]



Scheme 1.2 Cycloaddition reaction of CO₂ to epoxides to form cyclic carbonates.

A Lewis acid or Bronsted acid-based acid catalyst is necessary for the CO₂ cycloaddition reaction. The industry struggles greatly with the use of homogeneous catalysts since it is difficult and expensive to separate them from the reaction fluid. It becomes clear right away that having suitable heterogeneous catalysts with Lewis or Bronsted acidity is essential.

1.8 Mechanism of cycloaddition reaction of CO₂ to epoxides

The catalytic synthesis of cyclic carbonates from CO_2 using epoxide involve four steps, and they are discussed below along with a schematic representation of the entire mechanism in **Scheme 1.6**. Following are the four steps:

- 1. First, by a coordinative contact between the epoxide's oxygen atom and the Lewis acid aluminum site of the catalyst, the dual activation of the epoxide occurs quickly.
- The intermediate Al-coordinated bromo alkoxide is created when the nucleophile (Br-) from TBAB hits the less-hindered side of the epoxide in order to open the epoxy ring. Scheme 1.3



Scheme 1.3 Ring opening of the epoxide via nucleophilic attack.

 The production of a metal carbonate specie is then brought about by the intercalation of the CO₂ in the porous network into the abovementioned intermediate. (Scheme 1.4)



Scheme 1.4 Insertion of CO_2 into the Al-O bond

 The catalytic cycle is finally finished by an intramolecular SN2 cyclization, which yields carbonate and simultaneously releases Br while recovering Al-TMP-net. (Scheme 1.5)



Scheme 1.5 Cyclization via an intermolecular nucleophilic attack

The above steps are summarized in the Scheme below. (Scheme 1.6)



Scheme 1.6 Proposed mechanism for Al-TMP-net catalyzed cycloaddition of CO2 with epoxides.

Also, below is the way how tetrabutylammonium bromide (TBAB) with the cocatalyzes with the presence of a catalyst the conversion of an epoxide to a cyclic carbonate using CO_2 (Scheme 1.7)^[31]:



Scheme 1.7 Conversion of an epoxide to a cyclic carbonate catalyzed by TBAB.

By creating a hexa-coordinated complex between the oxygen atom of the epoxide and the core metal, cyclic carbonates are created. The Al-Cl bond of the catalyst's strength is lessened as a result of the creation of a hexa-coordinated complex. The Al-Cl complex's nucleophilic Cl atom favors interaction with the epoxide, resulting in the epoxide ring's easy cleavage. The bromo-alkoxide begins attacking the carbon atom of carbon dioxide at the same time that the extremely reactive anion of the quaternary ammonium salt TBAB catalyzes the opening of the epoxide ring by nucleophilic attack at the epoxide.

1.9 Current study

Recently, there has been a significant rise in interest in porous materials for gas purification, gas capture, and gas conversion. To address this, the current work offers a quick and easy method for creating highly cross-linked networks that have a substantial interior surface area and might be used to capture and convert carbon dioxide. The creation of highly cross-linked porphyrin networks using a standard free-radical polymerization technique is the main goal of this work. A tetra-methacrylate porphyrin derivative was made by reacting 5, 10, 15, 20-tetrakis (4-hydroxyphenyl)-21H, 23Hporphine with methacryloyl chloride in order to prepare the polymer networks. By using ¹H NMR spectroscopy, it was verified that the tetra-methacrylate porphyrin cross-linker had been made successfully. Using azobisisobutyronitrile (AIBN) as the initiator, the functionalized porphyrin with polymerizable methacrylate groups was further polymerized by free radical polymerization to create porous porphyrin networks (TMPnet). After that, the porphyrin ring underwent an usual metalation process to introduce aluminum ions (Al⁺³), creating networks of aluminum porphyrins (Al-TMP-net). Using a supercritical point drying technique, open pore samples devoid of solvent were obtained. SEM was used to analyze the morphology of the porphyrin and aluminum porphyrin network. N₂ adsorption-desorption measurements were used to explore the internal surface area of the porous network, and CO₂ adsorption capacity for both TMPnet and Al-TMP-net was assessed. Finally, in a cycloaddition process of CO₂ to epichlorohydrin, the catalytic performance and the recyclability of both TMP-net and Al-TMP-net was examined.

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2. Experimental

2.1 Materials

5, 10, 15, 20-Tetrakis (4-hydroxyphenyl)-21H, 23H-porphine (PO-(OH)₄, 95%), methacryloyl chloride (MCl, 97%, Fluka) and ethanol (absolute, 98%) were obtained from Sigma-Aldrich and N, N-Dimethylformamide (extra pure, 99.9%), triethylamine (synthesis grade, 99%), and tetrahydrofuran were purchased from Scharlau. 2,2'-Azobis(2-methylpropionitrile) (98%) was used as the initiator and was purchased by Acros Organics. Diethylaluminium chloride, 0.9 M solution in toluene was purchased by Acros Organics. (\pm)- Epichlorohydrin purum (\geq 99%) was used as the substrate in catalysis and was purchased by Sigma-Aldrich. Tetrabutylammonium bromide (TBAB) was used as a co-catalyst and was purchased from Sigma-Aldrich. The Tables below depict the chemical structures of the main chemicals used for the porphyrin functionalization and the cross-linkers and initiator used for the porous porphyrin networks synthesis.

Table 2.1. Chemical structures of the chemicals used for the synthesis of the tetramethacrylate porphyrin derivative.





Table 2.2 Chemical structures of the tetra-methacrylate porphyrin derivative and the initiator used for the synthesis of the porous TMP-net and of the aluminum salt used for the synthesis of Al-TMP-net.

2.2 Synthesis of the tetra-methacrylate porphyrin derivative

The esterification of PO-(OH)₄, with MCl, produced the tetra-methacrylate porphyrin derivative that served as a cross-linker for the creation of the Po networks. In a typical process, PO-(OH)₄ (0.518 g, 0.000763 mol) was dissolved in 40 ml dry THF. After stirring the above solution until all of the PO-(OH)4 had been dissolved, 6 ml (4.356g, 0.043 mol) of TEA was added. After that, MCl (0.8 ml, 0.0061 mol) was introduced into the above mixture dropwise at 0 °C. The reaction was kept at room temperature with constant stirring for the entire night. The triethylamine hydrochloride salt produced was removed from the reaction mixture the following day by filtration, while the excess TEA and THF were removed under reduced pressure.

The final product was dried under vacuum (0.3753 g, yield ~51%) and was characterized by ¹H NMR spectroscopy. ¹H NMR (300MHz, CDCl₃, δ) 2.82 (s, 2H), 2.23 (s, 12H), 5.91 (s, 4H), 6.56 (s, 4H), 7.54 (d, 8H), 8.22 (d, 8H), 8.90 (s, 8H).

2.3 Synthesis of porphyrin-based networks

The TMP-net was prepared by free radical polymerization. In a 22 ml vial, the tetramethacrylated porphyrin derivative (0.3753 g, 0.39 mmol) was first dissolved in 7 ml of DMFfollowed by the addition of AIBN (0.0026 gr, 0.00157 mmol). The reaction was then allowed to proceed for two days at 60 °C after the reaction mixture had been degassed for 20 min. DMF was used to wash away any crosslinker that had not yet reacted from the porphyrin network.

2.4 Synthesis of aluminum porphyrin-based networks

In a round bottom flask TMP-net (0.0712 gr, 0.0000744 mol) was dissolved in dry DMF and the solution was purged with N₂ for 30 minutes. Next diethyl aluminum chloride (Et₂AlCl 0.9 M solution in toluene, 0.1 ml, 0.000089 mol), were added while being constantly stirred under N₂ atmosphere. The reaction was kept at room temperature and stirred continuously overnight. After being purified with DMF the aluminum porphyrin network (Al-TMP-net) was recovered by centrifugation.

2.5 Preparation of porous TMP-net and Al-TMP-net by supercritical point drying (SPD)

For the drying procedure, a Bal-Tec CPD 030 critical point dryer was employed. Prior to drying, DMF where TMP-net was distributed and ethanol where Al-TMP-net was distributed was exchanged with liquid CO_2 for an extended period of time (8 h) at 8 °C using a plastic tube with two filters on either side. After leaving the sample at 41 °C and 91.3 bar for 2.5 h and gassing out for 55 min, CO_2 was finally removed under supercritical conditions to get the open pores TMP-net and Al-TMP-net networks.

2.6 Catalytic performance

The catalytic performance of the synthesized porphyrin-based networks were examined in the cycloaddition of carbon dioxide to epichlorohydrin. In TMP-net or Al-TMP-net, the catalyst, and TBAB, the co-catalyst, were then introduced to a 22 ml vial that had been purged with CO_2 for 20 minutes in the appropriate amounts. Next, 0.25 ml (3.2 mmol) of epichlorohydrin prior degassed with CO_2 was introduced to a vial that already contained 0.25 mol% catalyst and 2 mol% co-catalyst. The catalytic reaction was allowed to take place for 24 h at temperature ranging from to 100 °C. The conversion of epichlorohydrin to the carbonate was determined by¹H NMR spectroscopy.

2.7 Sample Characterization

2.7.1 Scanning Electron Microscopy (SEM)

Using a field-emission JEOL 7000 electron microscope operating at 10 kV, scanning electron micrographs were taken. The gel dispersion was diluted in ethanol before being dropped onto a silicon wafer and allowed to dry overnight in the air to create samples. To reduce charging during the experiments, a 10 nm Au film was sputter-coated onto the slides.

2.7.2 Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy

FT-IR spectroscopy is used to determine a material's chemical composition or whether a reaction is finished. In this study, FTIR spectroscopy was used to ascertain the chemical composition of the TMP-net and Al-TMP-net networks, depending on whether the aluminum ion was or was not absorbed into the porphyrin macrocycle. 128 scans were gathered for each spectrum during the measurements, which were conducted between 550 and 4000 cm⁻¹. Prior to each measurement, a background scan of 32 scans was captured and removed from the sample spectra.

2.7.3 Nuclear Magnetic Resonance (NMR) spectroscopy

The observations were performed in a 500 MHz Bruker ¹H NMR spectrometer at 300 K. To conduct the measurements, the materials were dissolved in deuterated chloroform (chloroform-d) and placed into an NMR tube.

2.7.4 Gas adsorption isotherms

A Quantachrome Model NOVA 3200e Gas Sorption Analyzer was used for the gas adsorption studies. The adsorbates chosen were the gases of nitrogen and carbon dioxide. The surface area of the samples was calculated from the gas adsorption data using the multipoint BET gas adsorption theory. The non-local Density Functional Theory (NLDFT) approach was used to calculate the samples' pore volumes. The samples were outgassed for 12 hours at 80 oC in vacuum prior to the measurement. While measuring CO2 adsorption at 273 K, the N2 isotherms were acquired using a liquid nitrogen bath at 77 K.

2.7.5 Diffuse reflectance UV/Vis spectroscopy

The solid networks' optoelectronic characteristics were investigated using diffuse reflectance UV/Vis spectroscopy. It is a Shimadzu UV-2401 PC UV/Vis Spectrometer that is being used. Measurements were made by depositing the powder sample on top of the BaSO4 base material, which serves as the reference material. The samples' reflectance was determined to be between 300 and 800 nm.

2.7.6 X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) was conducted on a SPECS spectrometer using a Phoibos 100 1D-DLD electron analyzer an A1 K α radiation as the energy source (1486.6 eV) and its was calibrated internally by the carbon deposit C (1s) (Eb = 284.6 eV).

3. Results and Discussion

3.1 Synthesis of the tetra-methacrylated porphyrin derivative

Methacryloyl chloride was used in an esterification reaction to functionalize the porphyrin molecule into a tetra-methacrylate counterpart. The esterification reaction was carried to a quantitative yield by using triethylamine to bind the HCl produced during the reaction and precipitated as a salt in the organic reaction medium (Scheme 3.1)



Scheme 3.1 Schematic representation of the synthesis of the tetra-methacrylate porphyrin derivative.

The successful synthesis of the tetra-methacrylate porphyrin derivative was confirmed by ¹H NMR spectroscopy (Figure 3.1). The porphyrin macrocycle's eight protons are allocated to the peak at 8.89 ppm, while the protons of the porphyrin's four phenyl groups are assigned to the peaks at 7.56 ppm and 8.22 ppm, respectively. The peaks at 5.91 and 6.55 ppm are the protons of the methylene group of the methacrylate groups, whereas the peak at 2.22 ppm is the twelve protons of the methyl groups of the integrated methacrylate moieties. Finally, the peak at -2.80 ppm correspond to the two protons of the two pyrrole rings of the porphyrin macrocycle. The ratio of the peaks H4,5 in respect to H1, show the full functionalization of the porphyrin.



Figure 3.1¹H NMR spectrum of the tetra-methacrylated porphyrin derivative in CDCl₃.

3.2 Characterization of the TMP-net and Al-TMP-net porous networks

By using Fourier transform infrared (FTIR) spectroscopy, the chemical composition of the TMP-net and Al-TMP-net networks was identified (Figure 3.2).



Figure 3.2 FTIR spectra of the TMP-net(black line) and Al-TMP-net(red line) network, (B) TGA of TMP-net and Al-TMP-net with a heating rate of 10 °C min.

The secondary amine bond, N-H, of the pyrrole ring was identified as the source of a vibration peak at 3313 cm⁻¹ in the FTIR spectra of the TMP-net network (Figure 3.2A). The C-H stretching mode from the pyrrole and benzene rings was assigned to the characteristic vibration peak at 2925 cm⁻¹. The vibration at 1742 cm-1 is assigned to the double carbon oxygen bond C=O of the ester. The porphyrin macrocycle and the benzene ring both displayed C=N and C=C stretching vibrations at 1669, 1500, and 1469 cm-1.^[1] With the exception of the peak at 1667 cm⁻¹, which was attributed to the vibration of the pyrrole ring's C=N bond and indicated the complexation of the aluminum ions by the porphyrin ring of TMP-net, the FTIR spectrum of TMP-net and Al-TMP-net were nearly identical.

The thermal stability of the polymers was determined by thermogravimetric analysis (TGA).TGA revealed that TMP-net and Al-TMP-net were both thermally stable up to $350 \text{ }^{\circ}\text{C}$ under nitrogen atmosphere (Figure 3.2B). As shown in Figure 3.2B, weight loss of 44% was observed for TMP-net while the Al-TMP-net exhibited weight loss of 45.28%. The small difference between the weight loss is due to the small percentage of the aluminum into the porphyrin with ~1.28% wt. It was inferred from this that TMP-net and Al-TMP-net had sufficient thermal stability to catalyze the CO₂ cycloaddition reaction.

The morphology o TMP-net and Al-TMP-net networks was determined by SEM. The SEM images in Figure 3.3 A and B show the morphology of the TMP-net and Al-TMPnet networks. SEM figure A shows the network formation and the porosity of the polymer before the aluminum addition while Figure B shows the polymer after the metalation.



Figure 3.3 (A),(B) SEM images of the TMP-net and Al-TMP-net network, respectively.

The surface compositions of TMP-net and Al-TMP-net were further investigated using X-ray photoelectron spectroscopy (XPS) analysis (Fig. 3.4A) and EDS analysis. For both TMP-net and Al-TMP-net, the XPS scan survey spectra clearly displayed peaks for carbon, nitrogen, and oxygen. N(1s) for TMP-net had binding energies of 397 eV and 394.7 eV, respectively, for pyrrolic N (-NH-) and aminic N (-N=). Furthermore, the XPS results verified that TMP-net was successfully metalated with Al(III). As shown in Figure 3.4B, an additional peak appeared in the Al-TMP-net spectra of Al2p_{3/2} with binding energy 68.1eV. By using the CasaXPS software the atomic percentage of Al2p into the porphyrin network was ~1.93% at (1.49% wt). Finally, to further confirm the existence of aluminium in Al-TMP-net, EDS studies were performed, verifying the successful metalation of TMP-net, by detecting aluminum into the sample.





Figure 3.4 (A) The XPS spectra of N1s of Al-TMP-net and (B) XPS spectra of Al2p of Al-TMP-net, (C) EDS analysis for the Al-TMP-net network.

The permanent porosity and surface area of the synthetic porous TMP-net and Al-TMPnet networks were determined. It was possible to acquire the open pore structure of the TMP-net and Al-TMP-net networks after solvent removal under supercritical conditions using liquid CO₂. The surface area of the samples was calculated using nitrogen adsorption/desorption measurements and the findings were analyzed using the BET method.

In order to determine the surface area of the samples, the nitrogen sorption measurements were analyzed using the BET method. The adsorption/desorption isotherms of TMP-net and Al-TMP-net are shown in Figure 3.5A. The Al-TMP-net network demonstrated a reduced BET surface area of $167m^2gr^{-1}$ with a total pore volume (V_{total}) of 0.26 cm³/g compared to the porous TMP-net network, which has a high BET area of $623 \text{ m}^2\text{gr}^{-1}$ and a total pore volume (Vtotal) of 0.70 cm³/g.



Figure 3.5 (A) Nitrogen adsorption/desorption isotherms at 77 K of the TMP-net and Al-TMP-net networks and (B) CO₂ adsorption isotherms of the TMP-net and Al-TMP-net networks at 273 K.

Adsorption isotherms were measured at 273 K to further assess the porous material's capacity to absorb CO₂ (Figure 3.5B). While the Al-TMP-net has a lower CO₂ adsorption capacity of 0.63 mmol/gr at the same pressure, the porous TMP-net network exhibits a greater CO₂ adsorption capacity of 1.54 mmol/gr at 990 mbar. Although we were expecting Al-TMP-net to exhibit higher adsorption capacity, it shows lower BET surface area and adsorption CO₂ capacity due to the different solvent used into the critical point dryer which was ethanol, which is a bad solvent for the polymer compared to DMF that was used for TMP-net.

3.3 Catalytic performance of the TMP-net and Al-TMP-net networks

The catalytic activity of TMP-net and Al-TMP-net was investigated in the cycloaddition reaction of CO₂ to epichlorohydrin to produce the cyclic carbonate under ambient pressure, at various reaction temperatures by varying the reaction time from 1h to 24h, and the molar ratio of catalyst to co-catalyst, while the reaction time and the molar ratio of catalyst to epichlorohydrin were remaining constant. The ¹H NMR spectroscopy was used to calculate the conversion of the reaction. The reaction mixture's ¹H NMR spectra reveal the emergence of new peaks corresponding to the protons of the cyclic carbonate, while at the same time, the peaks corresponding to the protons of epichlorohydrin are on the decline.^[2] A typical ¹HNMR spectrum of a catalytic reaction mixture is shown in Figure 3.6. The integrals of the proton peaks H₃ to the peak of proton Ha were rationed to determine the conversion yield.



Figure 3.6 A typical ¹H NMR spectrum of the reaction mixture using TMP-net as the catalyst.

Table 3 displays the reaction yield for three different temperatures at constant pressure(1atm) at 30, 80, and 100 °C. TMP-net and Al-TMP-net catalytic activity was contrasted with that of TBAB alone under the same reaction conditions and with that of the catalyst in the absence of TBAB.



Table 3. Cycloaddition of CO ₂ to epichlorohydrin to form cyclic carbonate at different reaction conditions ^a						
Entry	Catalyst	Co-catalyst	Temperature	Pressure	Time	Conversion % ^b
			(°C)	(atm)	(h)	
1	TMP-net	TBAB	30	1	24	31
2	Al-TMP-net	TBAB	30	1	24	21
3	-	TBAB	30	1	24	19
4	TMP-net	TBAB	80	1	24	65
5	Al-TMP-net	TBAB	80	1	24	60
6	-	TBAB	80	1	24	64
7	TMP-net	-	80	1	24	11
8	Al-TMP-net	-	80	1	24	0
9	TMP-net	TBAB	100	1	24	88
10	Al-TMP-net	TBAB	100	1	24	93
11	-	TBAB	100	1	24	82
12	TMP-net	-	100	1	24	21
13	Al-TMP-net	-	100	1	24	1
a. Read	ction conditions:	3.2 mmol epicl	hlorohydrin, cataly	st 0.25 mol %	with respect	to epichlorohydrin,

TBAB 2 mol% with respect to epichlorohydrin

b. Determined by ¹H NMR spectroscopy

As can be seen from Table 3, conversion rises as reaction temperature rises. In particular, for the TMP-net and Al-TMP-net networks, the conversion jumps from 31% to 88% and from 21% to 93%, respectively, when the temperature is raised from 30 °C to 100 °C. It should be noted that for these temperatures, the conversion for TBAB alone rises from 19% to 82%.



Figure 3.7 Conversion of the cycloaddition reaction of CO₂ to epichlorohydrin catalyzed by TBAB (■), TMP-net (●) and Al-TMP-net (▲) at different reaction temperature. Reaction conditions: Epichlorohydrin (3.2 mmol), 24 h, 1 atm, catalyst (0.25 mol%), TBAB (2 mol%).

Notably, at 30 °C, both the catalyst and the co-catalyst alone display low conversion yields, with the TMP-net yielding 31% (entry 1 in Table 3), the Al-TMP-net yielding 21% (entry 2 in Table 3), and TBAB yielding 19% (entry 3 in Table 3) conversion when the catalysts are not present. These findings demonstrate that the catalytic reaction is very slow at low temperatures. Following this confirmation, a temperature of 80 °C was used, which showed a higher conversion rate than the process at 30 °C. While the Al-TMP-net network and TBAB had conversions of 60% and 64% (entries 5 and 6 in Table 3, respectively) the TMP-net's conversion increased to 65% (entry 4 in Table 3). (entries 5 and 6 in Table 3, respectively). As shown in Table 3, control reactions using TMP-net and Al-TMP-net alone in the absence of TBAB as well as TBAB in the absence of any catalyst, including TMP-net or Al-TMP-net, were also conducted (entries 3, 6-8 and 11-13). These findings demonstrate the critical role played by TBAB in the cycloaddition of CO₂ to epichlorohydrin.

The amount of co-catalyst in the reaction medium was the second reaction parameter that was examined. At a reaction temperature of 100 $^{\circ}$ C, Table 4 displays the reaction conversion for two distinct concentrations of TBAB in relation to epichlorohydrin (1 and 2 mol %). The data indicate that the conversion significantly increased for all reactions when the moles of TBAB were increased from 1% to 2%.



Table 4. Cycloaddition of CO2 to epichlorohydrin to form the cyclic carbonate at different reaction						
	conditions. ^a					
Entry	Catalyst	Co-catalyst	Temperature	Pressure	TBAB	Conversion % ^b
			(°C)	(atm)	Moles %	
1	TMP-net	TBAB	100	1	1	64
2	Al-TMP-net	TBAB	100	1	1	69
3	-	TBAB	100	1	1	55
4	TMP-net	TBAB	100	1	2	88
5	Al-TMP-net	TBAB	100	1	2	93
6	-	TBAB	100	1	2	82
a. Reaction conditions: 100 °C, 1 atm, 3.2 mmol epichlorohydrin, catalyst 0.25 mol% with respect to						
epichlorohydrin						
b. Determined by ¹ H NMR spectroscopy						

Figure 3.7 demonstrates a very substantial rise in the conversion of epichlorohydrin for all catalysts the amount of co-catalyst increased from 1 mole% to 2 mole% with respect to epichlorohydrin, s. TMP-net had an increase in conversion from 64% (entry 1, Table 4) to 88% (entry 4, Table 4), whereas Al-TMP-net saw an increase in conversion from 65% (entry 2, Table 2) to 93% (entry 4, Table 4) (entry 5, Table 4). It should be observed that the conversion for TBAB alone increased from 55% (entry 3, Table 4) to 82% in the absence of any catalyst.



Figure 3.8 Conversion of the cycloaddition reaction of CO_2 to epichlorohydrin catalyzed by TBAB (\blacksquare), TMP-net (\bullet) and Al-TMP-net (\blacktriangle) for different amounts of co-catalyst. Reaction conditions: epichlorohydrin 3.2 mmol, CO_2 1 atm, 24 h, catalyst 0.25 mole%, temperature 100 °C.

Finally, a kinetic analysis utilizing 0.25 mol% catalyst and 2 mol% co-catalyst was carried out under 1 atm, at 100 °C, to further assess the catalytic behavior of the polymer networks. Table 5 displays the findings of the kinetic investigation.

			0//
	<u> </u>	1 atm	0~~
+	CO_2	Solvent free	ci0

Table 5. Cycloaddition reaction of CO ₂ to epichlorohydrin to form the cyclic carbonate. ^a						
Entry	Catalyst	Co-catalyst	Temperature	Pressure	Time	Conversion % ^b
			(°C)	(atm)	(h)	
1	TMP-net	TBAB	100	1	1	61
2	Al-TMP-net	TBAB	100	1	1	39
3	-	TBAB	100	1	1	58
4	TMP-net	TBAB	100	1	4	73
5	Al-TMP-net	TBAB	100	1	4	59
6	-	TBAB	100	1	4	74
7	TMP-net	TBAB	100	1	15	87
8	Al-TMP-net	TBAB	100	1	15	88
9	-	TBAB	100	1	15	78
10	TMP-net	TBAB	100	1	24	88
11	Al-TMP-net	TBAB	100	1	24	93
12	-	TBAB	100	1	24	82
13	TMP-net	TBAB	100	1	48	93
14	Al-TMP-net	TBAB	100	1	48	91
15	-	TBAB	100	1	48	76
 a. Reaction conditions: 100 °C, 1 atm, 3.2 mmol epichlorohydrin, catalyst 0.25 mol%, TBAB 2 mol% b. Determined by ¹H NMR spectroscopy 						

The above results show that the conversion of epichlorohydrin to cyclic carbonate occurs quickly within the first hour, with the TMP-net giving a 61% conversion (entry 1 in Table 5), the Al-TMP-net a 39% conversion (entry 2 in Table 5) and TBAB giving a 58% conversion (entry 3 in Table 5) in the absence of any catalyst. The reaction is complete for both catalysts in 24 hours. A typical conversion over time curve for the three catalytic processes is shown in Figure 3.8.



Figure 3.9 Conversion over time for the cycloaddition reaction of CO_2 to epichlorohydrin catalyzed by TBAB (\blacksquare), TMP-net (\bigcirc) and Al-TMP-net (\triangle). Reaction conditions: Epichlorohydrin 3,2 mmol, 100 °C, CO₂ 1 atm, catalyst 0.25 mol%, TBAB 2 mol%.

TBAB alone and the TMP-net network showed an increase in conversion to 74% (entry 6, Table 5) and 73% (entry 4, Table 5), respectively, after the reaction had been allowed to run for 4 hours. The Al-TMP-net, however, showed a lower conversion yield of 59% (entry 5, Table 5), indicating that the Al-TMP-net catalyst moves at a slower kinetic rate. With this knowledge, the catalysts were studied for a longer period of time. At 15 hours, it is evident that TBAB has begun to plateau with a conversion of 78% (entry 9, Table 5), but the TMP-net catalyst had a conversion of 87% (entry 7, Table 5) and the Al-TMP-net had an increase to 88% (entry 8, Table 5). Additionally, the reaction was allowed to run for 24 hours, and the conversion for TBAB was 82% (entry 12, Table 5), whilst the TMP-net conversion peaked at 88% (entry 10, Table 5) and the Al-TMPnet conversion was 93% (entry 11, Table 5). Last but not least, the behavior of the catalysts was studied over a longer period of time to see whether they had attained the highest conversion. Figure 3.8 illustrates that when used alone, TBAB after 48 hours shows a slight decline in conversion to 76% (entry 15, Table 5), whereas TMP-net yields a slight increase in conversion to 93% (entry 13, Table 5), and Al-TMP-net appears to have plateaued at 91% conversion (entry 14, Table 5). The above findings demonstrate that for both porous porphyrin networks, the catalytic conversion of epichlorohydrin to cyclic carbonate is maximized at 100°C, with the catalysts at 0.25% and the co-catalyst at 2% in respect to epichlorohydrin at 24h. Finally, the small difference between the catalysts conversion yield can be justified due to the small percentage of the aluminum into the porphyrin macrocycle.

3.4 Recycling experiments of TMP-net and Al-TMP-net

After the investigation of different parameters of the heterogeneous catalysis, recycling experiments were conducted in order to confirm the stability of the catalysts with the best catalytic activity after 5 runs of reusability. Tables 6 and Table 7 shows that the conversion yield remains almost constant after 5 times of the recovery and reuse of the catalysts.

Table 6. Catalytic reusability of TMP-net for the cycloaddition of CO_2 with epichlorohydrin. ^a					
Entry	Runs	Conversion % ^b			
1	1 st	88			
2	2 nd	84			
3	3 rd	83			
4	4 th	80			
5	5 th	77			
a. Reaction conditions: 100 °C, 1 atm, 3.2 mmol					
epichlorohydrin, catalyst 0.25 mol%					
b. Determined by ¹ H NMR spectroscopy					

Table 7. Catalytic reusability of Al-TMP-net for the				
cycloaddition of (CO ₂ with epichlorol	ıydrin.ª		
Entry	Runs	Conversion % ^b		
1	1st	93		
2	2nd	91		
3	3rd	90		
4	4th	89		
5	5th	89		
a. Reaction conditions: 100 °C, 1 atm, 3.2 mmol				
epichlorohydrin, catalyst 0.25 mol%				
b. Determined by ¹ H NMR spectroscopy				

As it is shown in figure 3.9, the metalated catalyst (Al-TMP-net) shows almost constant catalytic performance ~90% compared to the TMP-net that shows a slight decrease after 5 times of recovery. So, the stability of Al-TMP-net after 5 times of recovering and reusing it proves that the Lewis acid site Al^{3+} was stable in the polymer network.



Figure 3.10 (A) Recyclability test of TMP-net (B) and Al-TMP-net at 100 °C, 1 atm, 3.2 mmol epichlorohydrin, catalyst 0.25 mol% and cocatalyst 2%.

3.5 References

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4. Conclusions

In this thesis, porphyrin and aluminum porphyrin networks, which have potential to be used in gas capture and conversion applications, were successfully synthesized. Porphyrin network (TMP-net) was created using a straightforward free radical polymerization, whereas the Al-TMP-net was created by metalizing TMP-net with diethyl aluminum chloride. The successful metalation of TMP-net was verified by FT-IR, EDS and XPS analysis. SEM was used to examine at the networks' morphology. Supercritical point drying with liquid CO₂ was used to dry the samples from EtOH and produce solid open-pore gels. Using N₂ adsorption/desorption isotherms and the BET method, the networks' porosity and surface area were examined, and their ability to adsorb CO₂ was assessed using CO₂ adsorption measurements. After drying in supercritical CO₂, the TMP-net displayed a high BET surface area of 622 m²g⁻¹, whereas the Al-TMP-net displayed a reduced BET surface area of 167 m²g⁻¹. CO₂ adsorption studies revealed that the TMP-net exhibited an adsorption of 1.54 mmol/g at 273 K as opposed to the Al-TMP-net, which had an adsorption of 0.63 mmol/g at the same temperature. Thus, it may be said that the TMP-net network has a greater capacity to adsorb CO2 than the Al-TMP-net network, perhaps as a result of the former network's larger surface area. Furthermore, employing tetrabutylammonium bromide (TBAB) as a co-catalyst in the cycloaddition process of CO₂ to epichlorohydrin, the catalytic performance of both networks was assessed. Different temperatures, catalyst, cocatalyst quantities, and a kinetic analysis were all examined while investigating the catalytic activity of both catalysts. The results showed that the best conditions were at 100°C, for 24h with the catalyst at 0.25% moles and the co-catalyst at 2% moles in respect to epichlorohydrin. Finally, the recyclability at the same conditions of the two catalysts was examined showing the stability of both of the catalysts after 5 times of recovery and reuse.

Appendices

5. Characterization techniques

5.1 Scanning Electron Microscopy (SEM)

Even though it operates at low electron beam currents, the scanning electron microscope is built to deliver high-resolution, high-magnification images of a sample put on a surface. An electronoptical system concentrates the electrons that are emitted by a tungsten filament. By moving the beam across the surface in a sequence of parallel lines, the electron beam can scan the sample surface and yield composition at a spot, along a line, or over a rectangular area. The sample is fixed to a stage that can be precisely moved in all three planes (x, y, and z), perpendicular to the sample plane. Any kind of specimen can yield enlarged pictures using SEM. To generate the high energy electron beam required for imaging, the equipment typically runs in a high vacuum and an extremely dry atmosphere. Because of this, with a few notable exceptions, the majority of specimens used for SEM research are poor conductors. The imaging system of the SEM depends on the specimen having enough electrical conductivity to guarantee that the majority of incoming electrons travel to ground. Collecting the various signals that are scattered as a result of the high electron beam's interaction with the sample is necessary for the image to be created. Backscattered electrons and secondary electrons produced within the primary beam-sample interacting volume are the two main signals used to create pictures. While the secondary electron coefficient is largely insensitive to atomic number, the backscattered electron coefficient increases as the specimen's atomic number increases. The way samples may need to be prepared may need to change significantly as a result of this basic difference between the two signals.

When attempting to tie the identity, validity, and position of the chemical data back to the three-dimensional sample from which the information was acquired, as well as the form and structure of the two-dimensional images, the usage of scanning electron microscopy may be taken into consideration. Figure 5.1 shows a schematic illustration of a SEM setup.



Figure 5.1 Schematic representation of a typical SEM setup

5.2 ¹H NMR spectroscopy

An effective and widely used method for characterizing the structural properties of chemical substances is NMR spectroscopy.^[1] The most often utilized NMR techniques for characterization of materials are ¹H and ¹³C NMR. The foundation of NMR spectroscopy is the idea that positively charged nuclei spin on an axis while generating a weak magnetic field. An external magnetic field can either align with this nuclear magnetic field or oppose it (Figure 5.2).



Figure 5.2 (a)Random orientation of the nuclear magnetic fields in the absence of an external magnetic field (Bo), (b) Aligned or opposed nuclear magnet fields in the presence of an external magnetic field (Bo).

Varying nuclei absorb electromagnetic irradiation at different wavelength depending on the chemical and electrical surroundings. The NMR signal's position and pattern give the necessary details about the surroundings of the nuclei. Resonance occurs between the precise field intensity (in ppm) of a nucleus and a reference standard, often the signal from the deuterated solvent being employed. In contrast to nearby functional groups, which "deshield" the nuclei, electron clouds "shield" them from the external magnetic field, causing them to absorb at greater energy (lower ppm) (higher ppm). Equivalent nuclei in terms of chemistry and magnetism resonant at the same energy and produce a single signal or pattern. In accordance with the n + 1 rule and a coupling constant J, protons on adjacent carbons interact and "split" each other's resonances into multiple peaks. It is typical to see spin-spin interaction between nuclei separated by one, two, and three links. The protons of an NMR resonance can be estimated by integrating the area under the resonance, which is proportional to the number of nuclei that cause it.

5.3 Attenuated Total Reflectance (ATR)-FTIR spectroscopy

A sampling method used in conjunction with infrared spectroscopy is called ATR-FTIR spectroscopy. It is frequently utilized to check numerous materials, including solids, powders, pastes, and liquids, without further preparing them. When an object put atop a high refractive index crystal interacts with an infrared beam that is entirely internal reflected, changes in the infrared beam's properties are measured. ATR crystals are frequently made of germanium, zinc selenide, or diamond. The latter is a perfect material for ATR because of its great mechanical qualities. Pouring only a very small amount of a liquid sample onto the crystal's surface will do in this scenario. If the sample is solid, it is put in close proximity to the crystal. A high refractive index crystal is exposed to an infrared beam at a specific angle. Because of the characteristics of the ATRP crystal, the refractive index of the studied sample will be less than that of the crystal. Total internal reflection may take place at the interface of the two media under these circumstances at a specific angle of incidence. This internal reflection produces an evanescent wave that only penetrates a few microns into the sample after leaving the crystal's surface. The evanescent wave will be dampened in the infrared spectrum where the sample absorbs energy. The infrared spectrum of the samples is created after the beam is captured by a detector as it leaves the crystal.

5.4 Types of adsorption isotherms

Physical and chemical isotherms are the two categories of adsorption isotherms that have been distinguished. Adsorption isotherms, which are mostly caused by physisorption, come in a wide range of shapes, and the bulk of them fall under one of the IUPAC's six categories. The Brunauer classification refers to the first five categories (I through V). Physisorption isotherm type VI, a relatively recent form, was first listed in the IUPAC classification in 1985. (Figure 1.2a).^[2]



Figure 5.3 (A) main types of adsorption isotherms and (B) the four types of hysteresis loops based on the IUPAC classification.

Concave to the relative pressure (p/p0) axis is the type I isotherm. When the p/p0 is equal to 1, the isotherm curve hits a plateau. The isotherm curve rises dramatically for low relative pressure ranges. A constrained range of pore size can be inferred from the small range of relative pressure needed to reach this plateau. Additionally, the plateau's horizontal shape suggests a modest external surface area. As a result, the available micropore volume affects the limiting adsorption.

The Type II isotherm is initially concave to the relative pressure (p/p0) axis, before becoming linear and becoming convex to the p/p0 axis at high pressures close to 1. This formation denotes the presence of an adsorbed layer that has thickened over time. The uptake at point B (the start of the linear section), which marks the end of the monolayer and the start of the multilayer, is taken to symbolize these events if the isotherm's knee is acute. These isotherms, which enable unlimited monolayer-multilayer adsorption and complete isotherm reversibility, are achieved for non-porous or macro-porous adsorbents (absence of hysteresis). The Type III isotherm lacks a point B because it is convex to the relative pressure (p/p0) axis over the whole range. Since they are linked to weak adsorbent-adsorbate interactions, these isotherms are uncommon. Although type IV isotherms tend to plateau at high relative pressures, they are remarkably comparable to type II isotherms in the initial area. It displays a hysteresis loop that is typically connected to the capillary condensation that fills and empties mesopores. The upper branch reflects data obtained by progressive withdrawal, whereas the lower branch represents measurements obtained by gradual input of gas from the adsorbent. Although type IV isotherms are relatively frequent, there are four different types of hysteresis loops that can be classified for each system (Figure 1.2b). At low relative pressure, the Type V isotherm flattens out and becomes convex to the relative pressure (p/p0) axis. These isotherms are quite uncommon as type III. The hysteresis loop forms in accordance with pore filling and emptying mechanisms, and this isotherm type is linked to weak adsorbent-adsorbate interactions. Stepped isotherm, sometimes referred to as type VI isotherm, is a very uncommon phenomenon. Layer-by-layer adsorption on a very uniform surface is related to it. The system and temperature have an impact on how sharp the steps are. Capillary condensation is linked to hysteresis loops, which are typically recognizable and reproducible in meso-porous systems. Although there are many distinct types of loops mentioned in the literature, they are all primarily categorized by the IUPAC into four broad groups. A narrow loop of type H1 with almost parallel and perpendicular adsorption-desorption branches. Systems with a restricted distribution of uniform pores produce this kind of loop. The type H2 loop has a long, virtually flat plateau, a steep desorption branch, and is very broad. Materials having intricate pore structures that display interconnected pore networks of various sizes and shapes are used to create H2 loops. Since neither type H3 nor type H4 loops end in a plateau at high relative pressure, they are extremely similar. They are often produced by adsorbents or particle aggregates with slit-shaped pores, however in H4 loops, micropores are primarily responsible for the pore size distribution.

5.5 X-ray photoelectron spectroscopy (XPS)

X-ray Electron Spectroscopy for ChemicalAnalysis(XPS) is another name for Photoelectron Spectroscopy (ESCA). It is a method of surface characterization that may examine samples down to a depth of approximately 5 nm. Additionally, it can evaluate a variety of substances, including solids, gases, and liquids. In order to estimate the binding energy and identify the chemical elements that are present on the surface of the test sample as well as the chemical bond that unites these elements, this approach measures the photoelectrons' kinetic energy.

For the XPS technique to be able to eject electrons from the core and atomic orbitals, ultrahigh vacuum conditions (10-7 mTorr) are required. High energy X-rays (1000–1500 eV) are used as the radiation source. To gauge the energy of the emitting electrons, it makes use of an electron energy analyzer (photoelectrons). The binding energy and intensity of a photoelectron peak can be used to identify the elemental identity, chemical state, and quantity of a detected element. It varies from traditional methods of spectroscopy because electrons are detected instead of photons to look at the electronic structures of a material.



Figure 5.5 Schematic form of XPS

The photoelectric effect serves as the foundation for the fundamentals of photoelectron spectroscopy. Some electrons become energized enough to escape from the atom when

electromagnetic radiation bombards a sample. Photoelectrons are the expelled electrons. The following equations can be used to describe the photoelectric effect:

$$hv + E_i = E_f + E_k$$

$$\Rightarrow E_k = hv - (E_f - E_i)$$

$$\Rightarrow E_k = hv - E_I \text{ (Figure 5.4)}$$

Where hv is the X-ray photon's energy, E_i is the target atom's starting energy, E_f is the ionized atom's final energy, E_k is the photoelectron's kinetic energy, and E_I is the electron's ionization energy, or binding energy. The binding energy offers precise quantitative data about a molecule's electrical structure. The process of a neutral molecule changing from its ground state to an ion state is known as ionization ^{[3][4][5]}.

5.6 References

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