Summer 2018

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Recommended Citation

Almuslem, Ahmed Abdulghani, "Bifunctional porous polymeric fiber as a catalyst for N-Phenylglycine synthesis and carbonation of propylene oxide to propylene carbonate" (2018). *Masters Theses*. 7941.
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BIFUNCTIONAL POROUS POLYMERIC FIBER AS A CATALYST FOR N-PHENYLGLYCINE SYNTHESIS AND CARBONATION OF PROPYLENE OXIDE TO PROPYLENE CARBONATE

By

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A THESIS

Presented to the Faculty of the Graduate School of the
MISSOURI UNIVERSITY OF SCIENCE AND TECHNOLOGY
In Partial Fulfillment of the Requirements for the Degree

MASTER OF SCIENCE IN CHEMICAL ENGINEERING

2018

Approved by

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ABSTRACT

In this study, development of a polymeric bi-functional porous catalyst that can be used in various applications such as batch, packed-bed, and continuous flow reactors and the formation of highly important chemicals that have many applications in the industry. With this material many homogenous reactions can be conducted in heterogeneous environment which is more efficient and profitable. The catalyst was formed by grafting hollow fiber with APS then immobilized with Br using 1,2-dibromoprobane (Br/APS/PAI-HFs). The formed catalyst was tested with BET and FTIR to confirm the immobilization of Br. A porous polymeric material Br/APS/PAI-HFs provides the ability for ring opining of the propylene carbonate when it reacts with aniline to produce N-Phenylglycine in different reactors. Another, function to the catalyst is carbonation which is demonstrated when CO_2 reacts with propylene oxide in pressurized batch process to form Propylene carbonate with the purpose of continuing the reaction to produce N-Phenylglycine. The final part of this study is to demonstrate a continuous flow microreactor and to study the efficiency of the catalyst in such process compared to other reactors. The results show high conversion of aniline in batch reactor also a 100% conversion of propylene oxide in the first step of the batch system and +99% selectivity. For the continuous flow reactor, it appears to be very efficient to conduct such a process as the results shows high conversion and selectivity in such short time compare to the other two reactors.

ACKNOWLEDGMENTS

I would like to acknowledge every single person that helped in my academic career. First my advisor for his guidance, patient, and kindness. Second my committee members for their advices and help. Next, my lab mates for their help especially Yingxin He. And finally, my family and friends.

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1. INTRODUCTION

1.1. THE BEGINNING OF CATALYSIS IN THE INDUSTRY

Over the past few decades, catalyst development was the most important and secretive aspect to every catalysis reaction. Huge developments have been made in the past and continue to be made, companies are spending huge amount of money on catalysts developments to insure the best results and to minimize the environmental effects of catalyst. Having a sustainable, eco-friendly operation of production of chemicals, pharmaceutical, water desalination, biomass and more is the number one priority in this era. The history of catalysis goes back to the 1830s when Swedish scantest J. J. Berzelius wrote down on his publication he said “It is, then, proved that several simple or compound bodies, soluble and insoluble, have the property of exercising on other bodies an action very different from chemical affinity. By means of this action they produce, in these bodies, decompositions of their elements and different recombinations of these same elements to which they remain indifferent.”.[1] In 1875, the world firs catalysis process was launched to manufacture sulphuric acid and then changed to produce other chemicals.[1] Since then, the evolution of catalysis industry was evolving very rapidly to reach a stage that in every single chemical process that is running in the world it’s hard to be catalyst free. Many chemicals were used as catalysts back then, but the first one was platinum that has been used in 1838 by C. F. Kuhlmann.[1] A small theory back then was the back bone to the industrial revolution and a very important part of the human’s life that facilitate many aspects in mankind progress. Still the many of the catalytical processes are enigma, but science is evolving, and many researches are conducted to fully understand the beauty of such matter that can make an innovation in the industry.

1.2. TYPES OF CHEMICAL REACTORS IN THE INDUSTRY

The reactor is the heart of any chemical process and it's the most valuable equipment in the process. There are many types of reactors in the industry but all of those types branch out of three main types 1. Batch reactor, 2. Continuous stirred-tank reactor (CSTR), 3. Plug flow reactor (PFR). In this suction, each type of these reactor will be discussed.

1.2.1. Batch Reactor. Batch reactors are consist of a sealed vessel that guarantees that the volume of the reactor is constant. The laboratory batch reactors is a powerful tool that can be used to fully study the performance of chemical reactions under different temperatures and pressures. There are many designs of batch reactors, the vessel can be horizontal or vertical or the material used to build the reactor has to be strong enough to stand high temperature and pressure. Depending on the application that the reactor will use in the design chances. There are two modes for batch reactors:

1. Fully batch, which is very simple, reactants are inserted in the reactor and after reaction are done products are claimed at the end of the process.
2. Semi-continuous process, the reaction's kinetics play very important role so removing one of the products or reactants during the process sometimes is vital to reach equilibrium or to avoid run-away reactions.

Batch processes are commonly used in reactions that needs long reaction time and when a small amount of the product is desired also it is normally in liquid phase reactions. Pharmaceutical industry is the biggest user of the batch system. The advantages of batch system:

1. High conversion: due to long reaction time.
2. Cooling/heating processes are constant: jacket are used to heat and cool.
3. Produce many products.
4. Perfect small amount of product.
5. Cleaning is easy.

And the disadvantages are:

1. It needs many downtimes for cleaning.
2. It is hard to produce large amount in batch system.
3. Expensive, in terms of labor.

Many studies have used batch systems to understand the behavior of different reactions if it run under deferent temperature, pressures, reactor design also different types of catalyst are used in diverse batch systems.

1.2.2. Continuous Stirred-Tank Reactor (CSTR). Continuous stirred-tank reactor (CSTR) is open system reactor that the reactants flow to the reactor and reacts and flow out of the reactor continuously, the reactor operates in well mixing condition inside the reactor with steady state environment. The main idea of the of the CSTR is to generate a reaction system that is well mixed in order to conduct a reaction with uniform physical and chemical properties in every point of the reactor such as density and temperature. The main usage of CSTR is in pharmaceutical industry, petrochemical, but there are many other applications such as it is used in biological catalysis processes to produce different products that comes from breaking bonds of large molecules to form small ones for example methanol and ethanol. Also another uses are wastewater treatment, hydrocarbon processes which indicates how important CSTRs are in the industry. The advantages of CSTR system:

1. Temperature control is easy.
2. Cheep
3. Large capacity
4. Easy to enter the reactor

And the disadvantages are:

1. Low conversion
2. Deadzones, which are places inside the reactor where no mixing is occurring.
3. Bypass reactant, reactant can enter and leave the reactor without reacting if the outlet of the reactor is unsuitably located.

Many studies conducted on CSTR reactors to see how different structure, mixing techniques and many different parameters can affect the overall performance of the reactor.

1.2.3. Plug Flow Reactor (PFR). Tubular reactor or plug flow reactor is made of many tubes or pipes that the reactants flow through and react along their movement. Reactants are getting consumed and products are formed as they move toward the end of the reactor. PFRs have many uses in the industry in both gas and liquid phase which makes it very useful in many applications. Some of the uses of PFRs: oil cracking, sulfur dioxide oxidation, gasoline production, and ammonia synthesis. Small production of bioproducts such as algae can be produced by PFR but, normally PFRS are more about large scale production. Advantages of PFR system are

1. No moving parts, easily maintained.
2. High conversion.
3. Simple mechanics.
4. Consistency in product quality.
5. Efficient in terms of reactor volume.
6. Large production.
7. Low pressure drop.
8. Easy to clean.

And the disadvantages are:

1. Difficulty in controlling temperature.
2. Default to control.
3. Hot spots can take place when exothermic reaction in place.

Various studies have been conducted on PFRs and observations on the behavior of the reactor during different conditions. Different structures of PFRs are studied and optimized to conclude the best structure to each application.

1.3. CATALYSTS IN CHEMICAL PROCESSES

Catalysts in industry can be derived into two types homogeneous, and heterogeneous catalysts which they can be differentiated by how many phases exist in the reaction. Many reactions are consist of one phase only so the boundaries between solutions cannot be seen. In more details homogeneous and heterogeneous catalysis will be discussed.

1.3.1. Heterogeneous/Homogenous Catalyst. The norm for heterogeneous catalyst is for the reactants to be in different phase than the catalyst which is usually solid. When the reaction starts the catalyst starts an adsorption/desorption process where one or more reactants adsorbed into the active site the active sites may react with the reactant or help to weaken the bonds in order for the reaction to happen. When the reaction is done on the surface of the catalyst the product desorbed from the surface of the catalyst. Adsorbing the reactant for it to react and after reaction letting the product to desorb from the surface of the catalyst and not to remain on it is what makes a respectable catalyst. While in homogeneous catalyst all reactants and catalyst are in the same phase which is gas or liquid phase. There are many homogeneous catalyst reactions such as the solution oxidation reaction of persulfate ions with iodide in the presence of iron.

1.3.2. Heterogeneous vs Homogenous. The table below (Table 1.1) shows the differences between homogeneous reaction and heterogeneous reaction. There are many aspect to compare the two types of catalytical processes but the one mentioned are the ones that matter to this research. Many research have been done on this matter to come up with this results and to verify it.

Table. 1.1. Advantages and disadvantages of homogeneous and heterogeneous catalyst.

HOMOGENEOUS	HETEROGENEOUS
One phase	All phases
High selectivity	Low selectivity
Low temperature	High temperature
High diffusivity	Can be an issue
Difficult catalyst separation	Easy catalyst separation
Well defined active site	Poorly defined
Reaction mechanism well understood	Reaction mechanism poorly understood
Expensive recycling	Easy to recycle

1.4. SOME CATALYCAL SYSTEMS IN THE INDUSTRY

1.4.1. Packed-Bed Catalycal Reactor. One of the most famous reactor in the industry, they are used in every aspect from water desalination to pharmaceutical products. This usage of packed beds reactors is due to the high conversion per catalyst rate these reactor provide compare to other reactors. The processes that these reactors can applied to are diverse such as stripping, absorption, separation, distillation, and catalytic reactions. Advantages of packed-bed:

1. High conversion per catalyst unit mass.
2. Low operating coast.
3. Continuous.

Disadvantages:

1. Thermal gradients may exist.
2. Poor temperature control.
3. Channeling.
4. Difficult to clean.

The interests in packed bed reactors are still growing and new studies are still conducting to optimize processes that are running.[2]–[7]

1.4.2. Monolith Reactor. The use of monolithic support has increased where in the past it was only used in environmental application where low pressure drop is needed. Application used monolith reactor such as catalytic combustion, exhaust gas treatment, destruction of volatile organic compounds, and selective catalyst reduction. Nowadays, the interests in monoliths have increased when the process needs cost reduction and to be more efficient. These applications are mainly power generation, preferential oxidation, and oxidation of alkanes. Advantages of monolith catalyst system:

1. Low pressure drop.
2. High surface area.
3. No external mass transfer, no internal diffusion.
4. High selectivity.
5. Low plugging and fouling.
6. Easy to clean.
7. Easy to scale-up.

Disadvantages:

1. Difficult temperature control.
2. Heat travel from the monolith to reactor wall.
3. Non uniform flow.
4. High cost when scaled up to industry specifications.

Many studies focus on monolithic reactors because it has many advantages on the other reactors.[8]–[10], [10]–[12]

1.4.3. Inner Wall Catalycal Reactor. The use of inner wall catalyst is under lots of research, it has the ability to make the process more efficient and more interesting by enlarging the surface area to volume ratio. The way that this system works is the reactant travel from the shell side of the reactor to the inner wall of the catalyst moving through the pores of the catalyst providing more contact area. The advantages of inner wall catalyst

1. High conversion.
2. High selectivity.
3. High surface area to volume ratio.
4. Low cost.
5. Scale-up
6. Tune mass transfer resistance.

Disadvantages

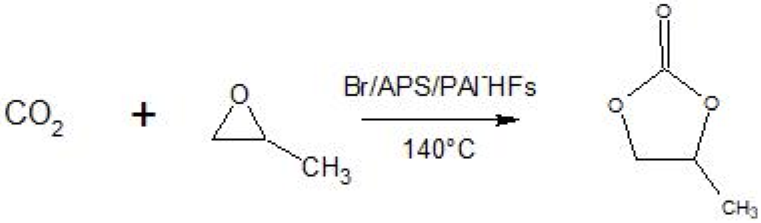
1. leaching
2. high pressure drop
3. Blockage.

There are not many research done on this matter because of its novelty, but there are some research that studied the immobilization of Pd(0) on hollow fiber and checked its performance in inner wall catalyst to study the behavior of the catalyst.[13]

1.5. CARBON DIOXIDE CABTURE/UTILIZATION

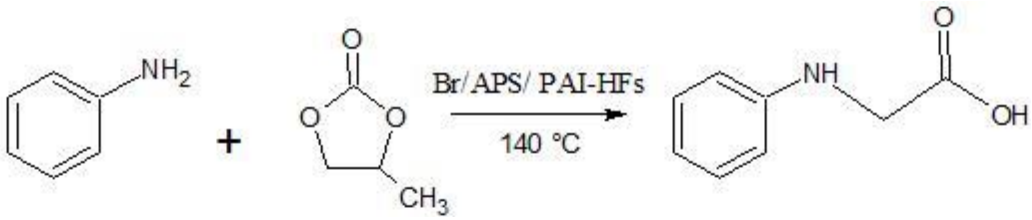
The reaction with CO_2 was recently studied as heterogeneous reaction of using ionic liquids. The reaction of carbon dioxide with propylene oxide that can lead to the formation of propylene carbonate.[14], [15] The amount of CO_2 on earth brings many challenges in utilizing it to produce many interesting products and creating a new industry using catalytical processes and CO_2 capture. Many processes have CO_2 in their reaction whether it was a production of CO_2 or a reduction of CO_2 to produce beneficial chemicals. Due to the stability of CO_2 all reactions of CO_2 must have a high energy for the reaction to go on by reaching level of driving force.[16]–[18] In the past, it was proved that catalysis can reduce the energy needed in order for the reaction to start and overcome many of the barriers that this problem generate. Over the years the reaction of CO_2 was used to produce many useful chemicals such as methanol, urea and more but the issue was that all reactions needed to be under high temperature and high pressure. One of the important reactions that utilize CO_2 is the carbonation of epoxides to produce cyclic carbonates which are very important chemicals in the industry.[14], [15], [19], [20] The synthesis of cyclic carbonate alongside polycarbonate is very significant in many fields to be used in many applications such as the formation of fuel additives and pharmaceutical. Many of the reactions in the past were using homogenous catalyst which brings issues in separating the product from the catalyst and the reactant which will well demand more energy and time to accomplish which may affect the entire process. Heterogeneous catalysts are also used in the formation of cyclic carbonates such as metal oxides, metal organic frameworks, and Porous organic polymers.[21] Many studies have discussed the use of amine nucleophilic substance such as Br^-, Cl^-, I^- and F^- and supported on a solid surface to act as bifunctional catalyst in cycloaddition catalytical processes.[22], [23] In this study the reaction of propylene oxide with CO_2 will be studied and reacted further in two steps reaction in pressurizes stirred batch reactor to form NPG as final product using hollow fiber as catalyst (Scheme 1.1),(Scheme 1.2).

First step



Scheme 1.1. Carbonation reaction of propylene oxide and carbon dioxide in a batch reactor to produce cyclic carbonate.

Second step



Scheme 1.2. Aniline and propylene carbonate react to produce NPG as second step in batch reactor.

1.6. BIFUNCTIONAL POROUS POLYMERIC CATALYST

Developing a material that has higher surface area to volume fraction which increase the efficiency of the process and more interesting. Furthermore, it can be scaled up and down as demanded and has a relatively low-cost polymeric material.[13], [24] a pseudo monolithic polymeric material hollow fiber have been used recently to demonstrate situ formation of hollow fiber as organocatalysts in both continuous flow and batch reactors. In this study, the catalyst used in this reaction is the hollow fiber (PAI-HFs) which is a new catalyst in this area and has enormous future in the industry, where it can be used in many reactions depending on the immobilized substance on it likewise water desalination and various processes. Many of the reactions in the industry are using liquid catalysts and there are many problems regarding the liquid catalysts regarding time and cost saving. This kind of material will have the solution to many of these problems and have promote the types of operation installed in the industry. Furthermore, the catalyst can be used in a batch reactor and in a continuous reactor likewise, which make it convenient on a large-scale process. This study focuses on synthesizing a porous material that can be used in batch reactor and continuous reactor. This polymeric material is used for CO_2 capture with the use of different mesoporous support such as ZrO_2, SiO_2 and TiO_2.[25], [26] The PAI-HFs is cross-linked to make them more applicable and has the resistance for solvent chemical used to for cross-linking is 3-aminopropyl trimthoxysilane (APS).[13] Br ions were successfully immobilized permanently in the reactor by creating a covalent bound with the APS/ PAI-HFs.[13] The study discussed the batch and continuous reactions with BR/APS/PAI-HFs.

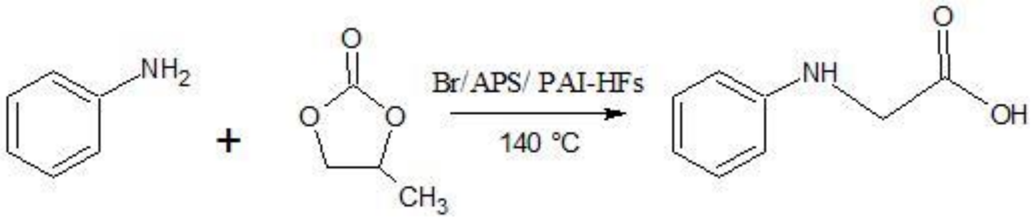
The use of halogens in catalytic reactions is very popular elements such as Cl, Br, and I are wildly used for several reaction processes.[14], [15], [19]–[21], [27], [28]

1.7. N-PHENYLGLYCINE (NPG) USES AND SYNTHISIS

N-Phenylglycine (NPG) is an amino acid and one of the important substances in the industry and involves in many of the high technology and developments in many areas due to its properties of environmentally friendly and nonallergic, and when it is joined with its derivatives applications of various fields can be applied. NPG is used as photoinitiator to initiate free radical reaction in polymerization due to its ability to photodecomposition under UV LED.[29] The use of NPG as dyeing agent in polymerization where it produced a significant charge when it is combined with salt to initiate free radical reaction under irradiation conditions.[3] NPG is also used as anti-inflammatory substance in the medical sector due to its economical worth and safety and the idea behind that is to form a bifunctional chemical that can mimic the role of amino acid to elevate the properties of the chemical by developing biological and physicochemical properties that support aim of that chemical.[31] Another uses of NPG is to enhance capability of Cu^{+2} adsorption, it is proved that NPG after it goes under free radical polymerization process (Poly N-Phenylglycine) the adsorption capability of PPG is increased after deprotonation precess.[32] The importance of NPG can reach many applications, a research was done that proves that NPG can be used as tooth tissues due to its physical properties such as tensile strength.[33], [34] Forming a product with many derivatives that can be used in many applications is essential when it comes to industry and profits generation. So, the product is highly used in various sectors and developments on this type of material and using it in new segments are growing to reach many innovations.

1.8. CONTIONOUS REACTION USING BIFUNCTIONAL HOLLOW FIBER

Continuous-flow reactors has seen big innovation regarding lab scale equipment with many researches are done on this type of flow reaction, the interest of the industrial companies in this type of reactions increases to maintain a sustainable, economic and environmentally friendly of the production of pharmaceuticals, biomass, biochemicals, and water desalination to increase the efficiency of the unit[35]–[45] Many researches have these ideas to apply continuous flow reaction with different types of surfaces and materials. Researches have been done on various reactions with different type of surfaces. Metal nanoparticles have been immobilized in many reactions, elements like nickel, copper and ruthenium were implemented on solid surface such as polymers and oxides to provide a very efficient catalytical system which elevate and uses the properties of flow chemistry and nanoparticles.[46]–[48] Pd(0) and Pd(II) were successfully immobilized on many surfaces in the past.[37], [49], [50] Many approaches have been developed in the study of nanoparticles where different types of materials have been immobilized on different surfaces. For continuous flow reactor the type of reactor can be discussed on three main concept 1. Inner-wall catalyst; 2. packed-bed; and 3. Monolithic flow-through. In packed-bed reaction, it is more common for the reaction to result in low efficiency, low selectivity, hot spot formation and uncontrolled flow in the reactor. However, in packed bed microreactors, there is a very high ratio between active catalyst and reagents and that’s due to flowing through packed bed. The turnover numbers are higher in packed compared to a batch reactor due to the higher concentration of the catalytical material inside the reactor which also enhances mass transfer and lead to a higher reaction rate.[42], [51]–[53] Another possible choice is the monolithic reactor which uses different materials such polymer, alumina, and titania, where in this type of reactor the disadvantages of packed-bed reactor are to be overcome.[54]–[57] Monolith is a hierarchical, well-defined porous material that different types of materials can be immobilized on it. With every type of reactors there are some concerned associated with the monolithic microreactor: 1. Clogging, which usual happen in inorganic materials, that are very expensive to buy, and it is very fragile, where it happen inside the channels of the monolith when the insoluble solid particles participate inside the channel; 2. Swelling, which happen when the monolith is made of organic material.[40], [56]–[59] Batch reactors are wildly used in the pharmaceutical processes and with all the drawback with batch system which are frequent startups and shutdowns which will waste time, cleaning between every batch, there is no consistency between batches, and not the best idea for mass production.[13] So, the idea of having a powerful, continuous, catalytical system that has a better efficiency and selectivity than the batch process will be a major development in the pharmaceutical industry. One major disadvantage of the continuous flow in microreactors is leaching of the catalytical particles from the support which will result in contamination of the product, catalyst loss, and ultimately lower efficiency. Catalyst can be very critical sometimes so even a small amount of the catalytical particles can make an essential change in conversion and selectivity. Consequently, a thorough understanding in the catalytical reactions and catalysts knowing the mechanism and how the bound are formed is essential to the permanent immobilization of many types of chemicals which could bring a solution for leaching of the catalyst and provide a very stable catalyst. In this study the reaction of aniline with propylene carbonate to produce NPG will be discussed in a continuous flow reactor using the same catalyst Br/APS/PAI-HFs (Scheme 1.3).



Scheme 1.3. Aniline and propylene carbonate react in a continuous flow reactor to produce NPG.

1.9. METHOD

The synthesis method used in this reaction is mix propylene carbonate with aniline in the present of the catalyst to produce NPG. The use of permanent immobilization of different types of catalysts on a porous polymeric material that address the stability of the catalyst, reactivity of the catalyst, and the recyclability of the catalyst is a new research that has not been investigated or it has lack of research. The idea of a polymeric porous material, hollow fiber, has been introduced recently that helps the chemical heterogeneous and homogenous reaction. Based on the research done on hollow fiber a hypothesis has been done that a very supportive polymeric catalyst can be generated from hollow fiber, support and catalytic chemical that can provide an enormous catalyst that can solve many of the difficulties and drawback of the homogenous catalytic processes. The attractiveness of a catalytical process is based on the ratio of surface area to volume, tuning mass transfer resistance, and the ability to be scaled-up which can be provided with the use of a pseudo monolithic material, hollow fiber, that it can create a very efficient system. This type of material that is relatively inexpensive can be utilized on a large-scale application to provide clean, and efficient chemistry due to the recyclability and the properties of the hollow fiber that provides a well-defined catalytic system. Different approaches of the reactions have been done the first one is in packed bed system in rounded flask then in a batch system with compressed carbon dioxide and propylene oxide to produce propylene carbonate and add it to aniline to produce NPG and the last one is in a continuous flow system where a microreactor was built to demonstrate this type of reaction on a lab scale. The reaction is done several times with different reaction time and different hollow fibers as catalyst. Different fibers are used to study the effect of each fiber on the conversion and to optimize the reaction condition. The bare hollow fiber (PAI-Hfs) was crosslinked with 3-aminopropyl trimthoxysilane and then followed by an alkylation process with 1,2-dibromoprobane to immobilize bromine on the surface of the catalyst. Analysis of the product was done by the GC-MS, NMR, and FTIR.

3. EXPERIMENTS

2.1. CHEMICALS

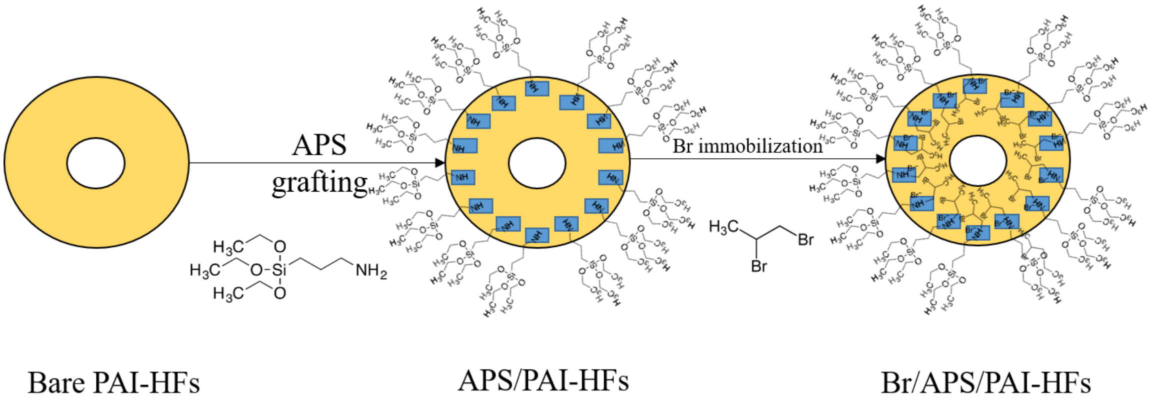
In this study, different chemicals have been used. Methanol, toluene, (3-aminopropyl) triethoxysilane (APS), 1.2 dibromopropane, aniline and propylene carbonate were all purchased from Sigma-Aldrich Chemistry.

2.2. PROCEDURE OF (APS) GRAFTING OF THE HOLLOW FIBER

The hollow fiber will be cut into convenient pieces that fits the reaction condition. The hollow fiber will be socked with methanol 60-80 ˚C for four hours in round bottom flask. Aminopropyltriethoxysilane (APS) is mixed toughly with Toluene in a rounded bottom flask in a ratio of 1:9 (10% of APS in Toluene). The hollow fiber is placed into the mixture, 4 drops of water added and stirred very well on an oil path for 12 h under 80 ˚C. Finally, the hollow fiber is placed in a vacuum oven for four hours.

2.3. PROCEDURE OF Br IMMOBILIZATION ON THE FIBER

In a normal procedure to immobilize Br on the APS/PAI-HFs, toluene (40 ml) is mixed with 1.2 dibromopropane (10 ml) and placed in rounded flask with the fiber. The mixture with the fiber is stirred for 6-8 h in an oil path with 80 ˚C then the hollow fiber is separated from the mixture. The hollow fiber is let to dry overnight and then placed in a vacuum oven for 4 h to remove the toluene residues on the fiber. Surface area and pore volume were calculated using Brunauer-Emmett-Teller (BET) using the isotherm data and Barrett-Joyner-Halenda (BJH) method.



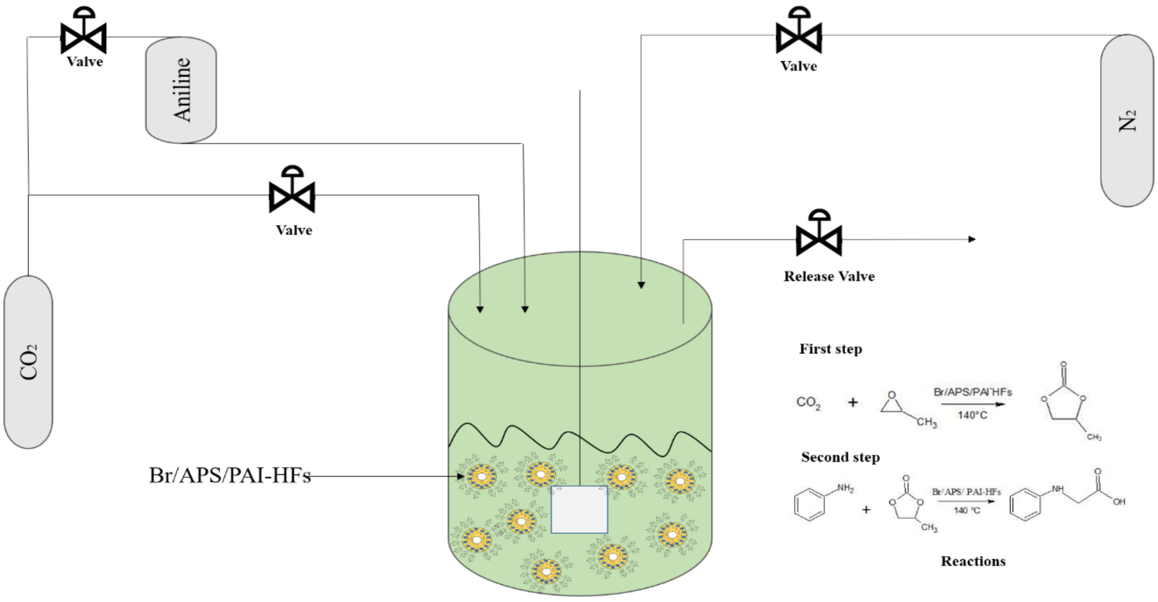
Scheme 2.1. Process of grafting APS and immobilization of Br $^{-}$ on hollow fiber.

2.4. SYNTHESIS OF *N*-PHENYLGLYCINE IN BATCH REACTOR

In a standard procedure of synthesis, propylene carbonate (40 ml) is mixed with aniline (8 ml) and curried out in 100 ml rounded bottom flask in oil path. Br/APS/ PAI-HFs (0.5 g) is added to the mixture. The reaction is curried under 140 ˚C and ambient pressure. The temperature was let to be stable and then the timer was started to collect samples in different times, the reaction was put to run for 72 hours to examine the conversion and selectivity of the product. Samples were taken and filtered every hour for analysis where methanol was used as solvent in GC-MS. The reaction mixture was analyzed by H NMR, FTIR and GC-MS.

2.5. SYNTHESIS OF *N*-PHENYLGLYCINE IN PRESSURIZED REACTOR

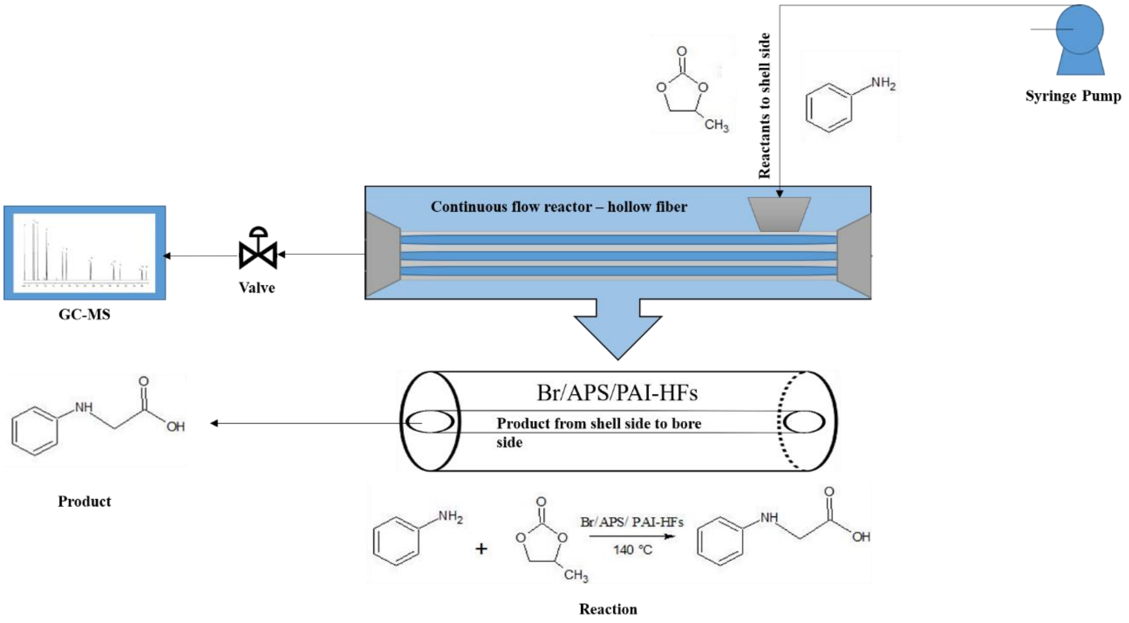
To examine the catalyst in a different reaction a two stages reaction was curried in a pressurized stirred batch reactor using hollow fiber (Br/APS/PAI-HFs). The reaction first stage, propylene oxide (40 ml) and 0.5 g of the catalyst were mixed and react for one hour to produce propylene carbonate. The reaction went throw a 100% conversion, then on the next step aniline (8 ml) was introduced to the reactor using pressurized carbon dioxide and purged using compressed N_2 then the reaction proceeded and NPG to be produced. The reaction was under 140 ˚C and 50 bar of carbon di oxide. When the reaction started we waited for several minutes to ensure that there is no leakage and the temperature to be stable. The reactor was let to run under continuous watch for 9 hours. After the reaction finished the reactor was turned off and the reactor was let to cool down and then depressurizes from carbon dioxide then the product was analyzed.



Scheme 2.2. Schematic representation of the pressurized batch reactor.

2.6 SYNTHESIS OF *N*-PHENYLGLYCINE USING CONTINUOUS FLOW

To examine the activity of the catalyst of the hollow fiber (Br/APS/PAI-HFs), a continuous flow reaction was curried in a microreactor assembled in the lab. Stainless steel model was built containing three hollow fibers at 140 ˚C. the microreactor was heated by a heating tape and covered with jacket to fix the temperature and minimize loss of heat. A mixture of the reactant was prepared (propylene carbonate: aniline, 5:1 ratio) and pumped into the reactor using a syringe with a flow rate of 0.03 cm^3 min^{-1}. The mixture was introduced in one inlet (T-junction) on the shell side of the fiber. The reactor was designed for the reactants to exit the reactor from the hollow side and to be collected from the outlet of the reactor using a valve. The reactor left for half an hour for the temperature to be stable and then samples were collected in different times.



Scheme 2.3. Schematic representation of the continuous flow reactor using hollow fiber.

3. RESULTS AND DISCUSSION

3.1. PRODUCT ANALYSIS

The reaction of propylene carbonate and aniline in the present of Br/APS/PAI-HFs was performed with different conditions to investigate deferent reaction aspect. Reaction times and deferent hollow fiber types, which differ in diameter, were investigated and the product was analyzed by NMR, FTIR (Figure 3.1) (Figure 3.2) and GC-MS to ensure the structure of the product and to see the conversion and selectivity of NPG in various conditions. H^1 NMR was conducted on all Product samples, the H^1 NMR shows that the product appears in all samples, but it needed more confirmation. So, the FTIR (Figure was conducted and confirms many functional groups of the product and shows strong indication of the product presence. After H^1 NMR, FTIR, and GC-MS was conducted on all product samples and the GC-MS prediction confirms the product presence and determine the conversion, selectivity and yield of NPG. a calibration curve was generated to determine the conversion of aniline. The calibration curve starts from the maximum concentration of aniline in the reaction mixture which is 5400 ppm and ends with a 83 ppm for a total of 10 points.

3.1.1. Packed Bed Reaction of Aniline and Propylene Carbonate with 28 Br/APS/PAI-HFS. Reaction time is one of the significant factors in this research, in the 28 Br/APS/PAI-HFs, as it appears from the graph the conversion of aniline is increasing with time. After one hour the conversion of aniline was 31.47% with selectivity of NPG 74.09 and yield of 23.32% (Table 3.1) which indicate that there are several intermediate products as it shows from the GC-MS and the reaction did not reach the optimum state.

When analyzing the 4 hours sample it was concluded that the conversion slightly increased, but the selectivity and yield of NPG increased sharply to indicate that after 4 hours the reaction is in stable conditions. After 9 hours the reaction seems to reach its best states regarding conversion and selectivity 32.43% and 99.35% (Table 3.1). It can be seen from the table that when time increases the conversion of aniline is increasing with time with acceptable selectivity percentage of NPG. The reaction let to run for 72 hours and when examining the results, it appears that while conversion increases the selectivity and yield decreases, because the reaction started to generate many side products that appeared in the GC-MS analysis. Overall the conversion of the aniline is increasing with time is it can be noticed form (Figure 3.3) (Figure 3.4).

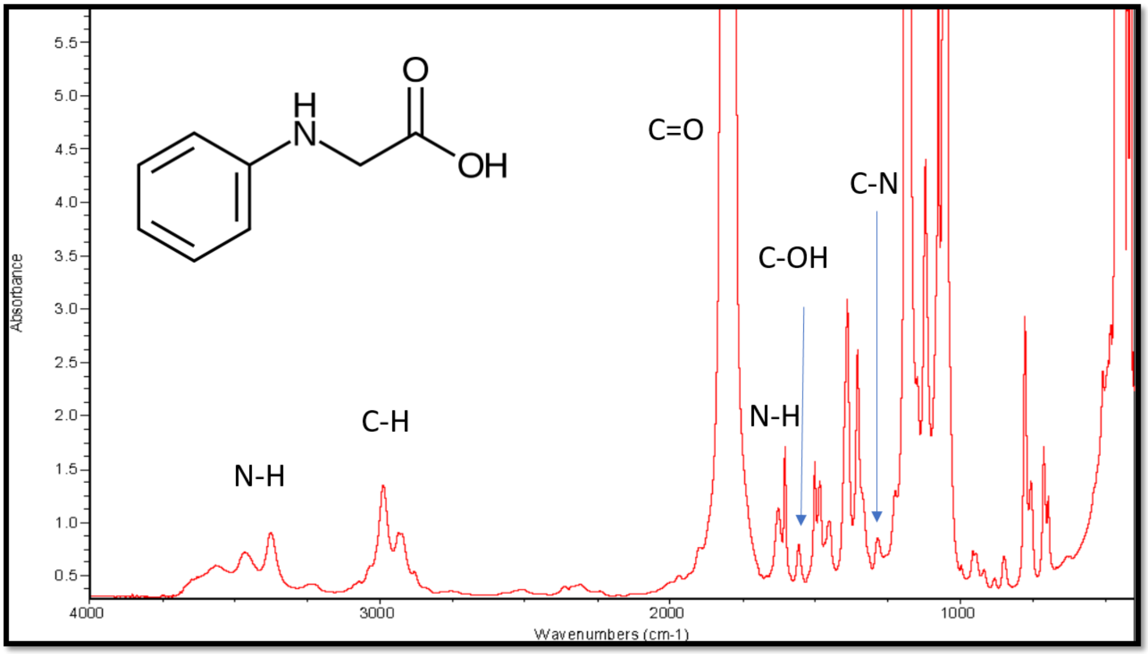


Figure 3.1. Analysis of FTIR result of the product

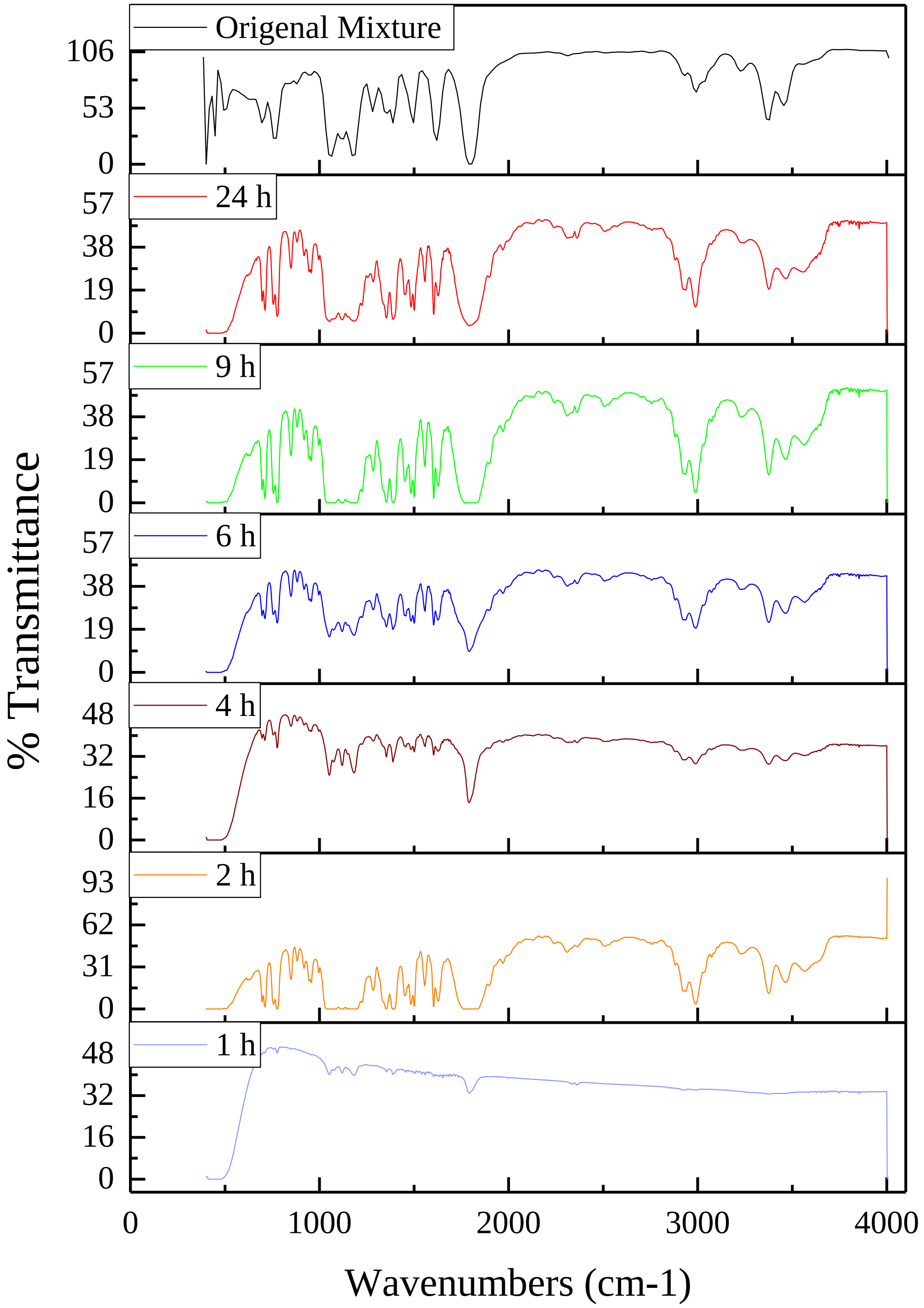


Figure 3.2. FTIR result of the product in different times

Table 3.1. Reaction of aniline with propylene carbonate with 28 Br/APS/PAI-HFs.

Reaction Time (h)	Conversion of Aniline (%)	Yield of Product (%)	Selectivity of the product (%)
1	31.47	23.32	74.09
2	31.87	38.48	98.96
4	32.26	31.99	99.15
6	32.35	29.52	98.33
9	32.43	32.22	99.35
24	47.01	44.68	95.05
48	51.79	47.61	91.92
72	62.12	51.60	83.08

Reaction conditions: aniline: 2 mmol, propylene carbonate: 10 mmol, 28 Br/APS/PAI-HFs: 0.5 g.

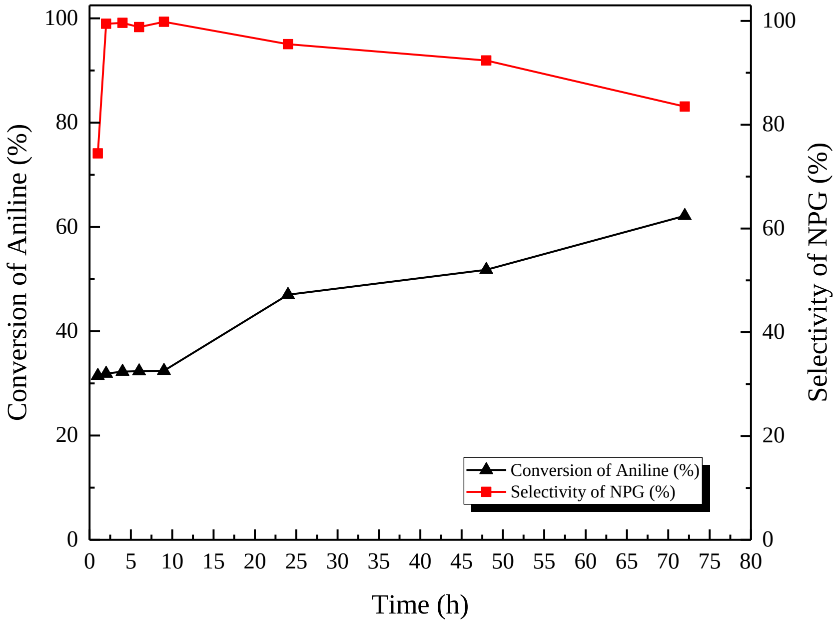


Figure 3.3. Effect of reaction time. Reaction conditions: aniline: 2 mmol, propylene carbonate: 10 mmol, 28 Br/APS/PAI-HFs: 0.5 g.

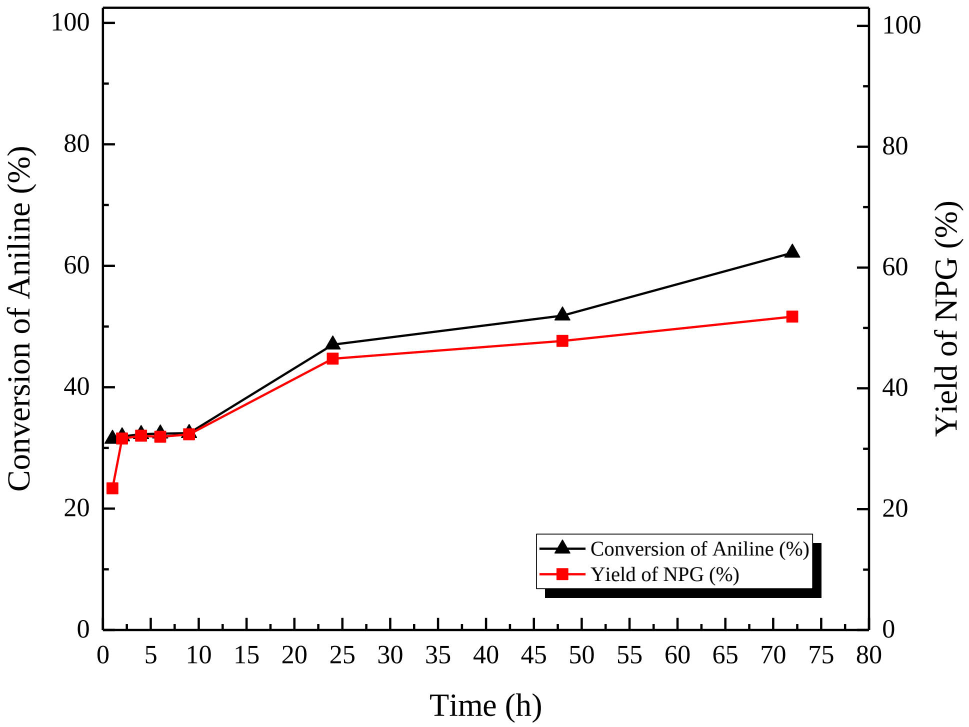


Figure 3.4. Effect of reaction time on yield. Reaction conditions: aniline: 2 mmol, propylene carbonate: 10 mmol, 28 Br/APS/PAI-HFs: 0.5 g.

3.1.2. Packed Bed Reaction of Aniline and Propylene Carbonate with 33 Br/APS/PAI-HFS. When the same reaction was conducted with 33 Br/APS/PAI-HFs with same conditions the results shows that a higher conversion is achieved in shorter reaction time which indicates that the efficiency of the 33 Br/APS/PAI-HFs is higher when it is compared to 28 Br/APS/PAI-HFs. When analyzing the one-hour sample it shows that the conversion of aniline to NPG is 41.30% and the selectivity was 94.39% (Table 3.2) which is higher than the previous catalyst. The conversion is increasing with time and it reached 47.05% after 6 hours with high selectivity of 98.53% (Table 3.2). After 9 hours the conversion of aniline has reached 48.58% with 48.16% yield and

98.58% selectivity (Table3. 2) and when it is compared to the 28 Br/APS/PAI-HFs such numbers are achieved after 24 hours. Also, the conversion reached 80.99% after 48 hours with 64.36% yield and 79.47 selectivity (Table 3.2). Overall, 33 Br/APS/PAI-HFs shows much better results than the 28 Br/APS/PAI-HFs whether it is higher conversion and shorter time to reach optimum state (Figure 3.5) (Figure 3.6). So, the 33 Br/APS/PAI-HFs will be used in the batch reactor and the continuous flow reaction.

Table 3.2. Reaction of aniline with propylene carbonate with 33 Br/APS/PAI-HFs.

Reaction Time/h	Conversion of Aniline (%)	Selectivity of the product (%)	Yield of Product (%)
1	41.03	94.39	38.73
2	42.53	97.47	41.45
4	44.94	97.69	43.90
6	47.05	98.53	46.36
9	48.85	98.58	48.16
24	64.92	90.38	58.67
48	80.99	79.47	64.36

Reaction conditions: aniline: 2 mmol, propylene carbonate: 10 mmol, 28 Br/APS/PAI-HFs: 0.5 g.

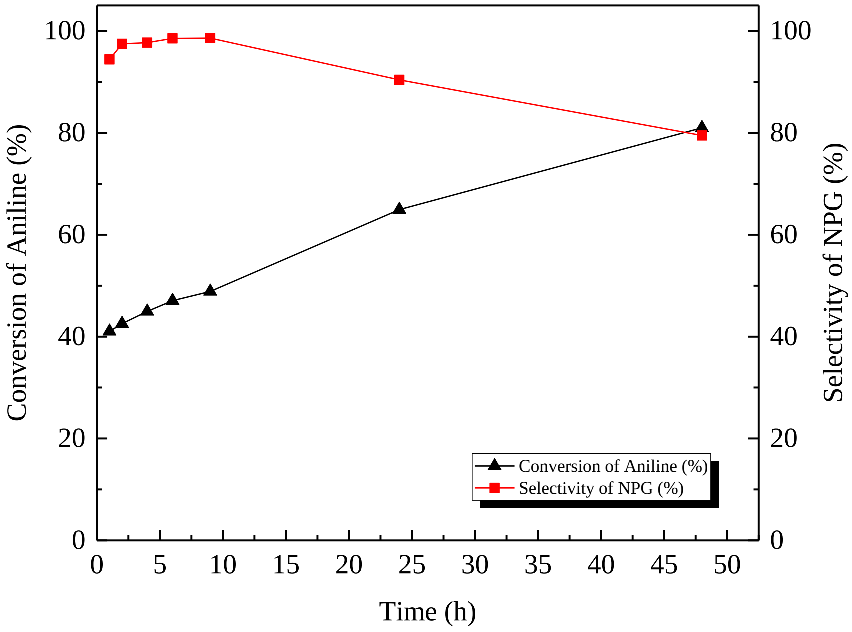


Figure 3.5. Effect of reaction time. Reaction conditions: aniline: 2 mmol, propylene carbonate: 10 mmol, 33 Br/APS/PAI-HFs: 0.5 g.

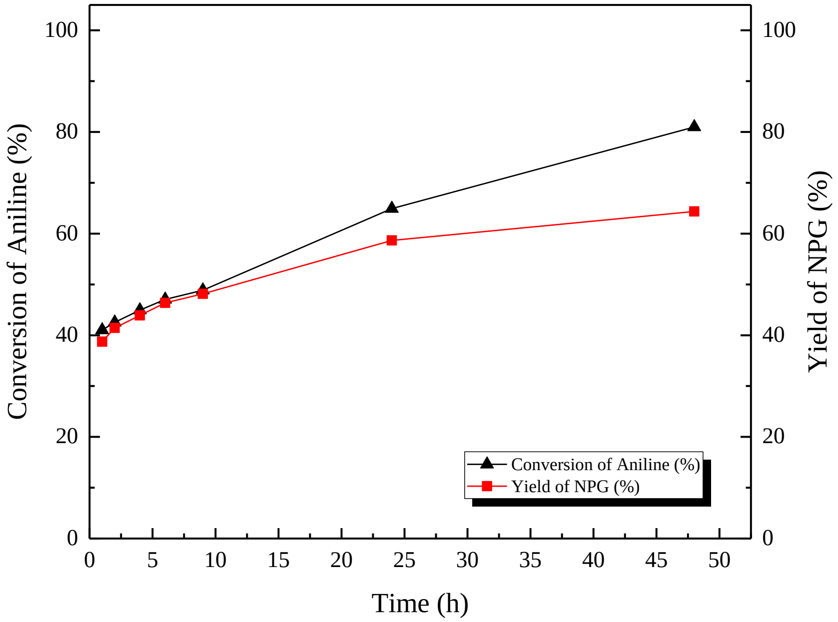
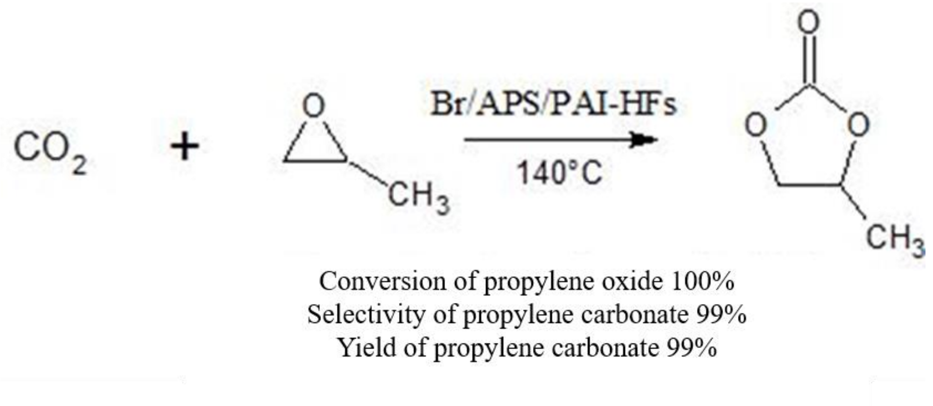


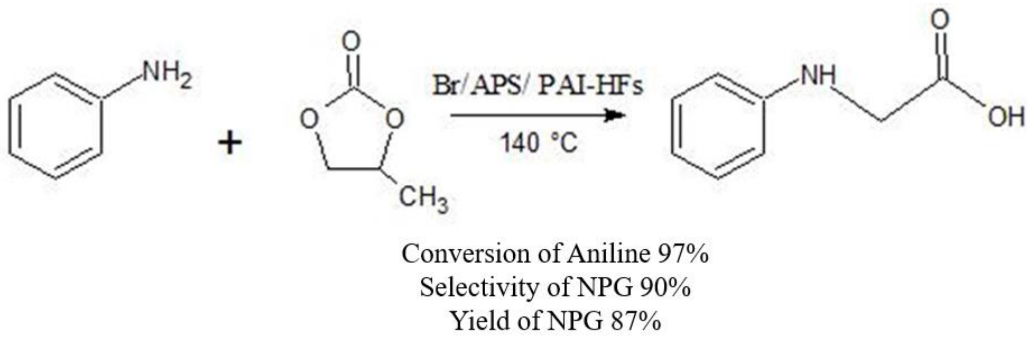
Figure 3.6. Effect of reaction time on yield. Reaction conditions: aniline: 2 mmol, propylene carbonate: 10 mmol, 33 Br/APS/PAI-HFs: 0.5 g.

3.1.3. Pressurized Batch Reaction of Co$_2$, Aniline and Propylene Oxide with 33 Br/APS/PAI-HFS. In two steps batch reaction, the products were confirmed by H NMR, FTIR, and GC-MS and analyzed. The steps of these two reactions are first to let propylene oxide and CO_2 reacts to form Propylene carbonate which is used as reactant in the second reaction with aniline. Running for 2 hours, maximum conversion of propylene of 100% and 99% selectivity (Scheme 3.1) which is high number compared to other research that have been done before. Also, for the second step of the reaction and after 9 hours, a 97% conversion of aniline was formed with 90% selectivity and 87% yield of NPG (Scheme 3.2). The higher numbers compared to the packed bed reaction may resulted due to the purging process which eliminated the existence of air that may decrease the reaction rate and generate side products in the reaction. The results are showing promising numbers that can be used in the future industry as main process to produce cyclic carbonates or NPG.



Conversion of propylene oxide 100%
Selectivity of propylene carbonate 99%
Yield of propylene carbonate 99%

Scheme 3.1. The results of carbonation reaction of propylene oxide and carbon dioxide running for 2 hours in the first step of a batch reactor to produce cyclic carbonate.



Conversion of Aniline 97%
Selectivity of NPG 90%
Yield of NPG 87%

Scheme 3.2. The results of aniline and propylene carbonate react in a second step of batch reactor running for 9 hours showing conversion, selectivity and yield.

3.1.4. Continuous Flow Reaction of Aniline and Propylene Carbonate with 33 Br/APS/PAI-HFS. One of the novel ideas is the use of micro reactors in labs to synthesize chemicals and after going throw the packed-bed reactor and batch reactor, the study of the continues flow reaction came to mind. So, the reaction was done in the same conditions such as the packed-bed reaction but this time it was aimed that the reactant travel from the shell side of the catalyst to the porous side and collected from the hollow side. The results of this experiments show high efficiency of the catalyst compared to other reactions packed bed reaction in very short time and as data shows after only 5 minutes of reaction time a conversion 30% was achieved with 97% selectivity and 29% yield which indicates a much high efficiency for this process. The reaction was let to run for two hours and the end result was 60% conversion and 97% selectivity and 59% yield. (Table 3.3) To predict the final result after 9 hours the conversion will achieve 100% and the selectivity will reach +99%. The reasons for these results are the structure of the hollow fiber and the process that the reactant was forced to travel from shell side through pours to the hollow side and exit which will maximize the contact area with the active site on the catalyst. Another reason could be the lack of air components in the process such the batch reactor, because the way the setup of the continuous microreactor is ensured that air cannot get into the process. Overall the conversion is increasing with time (Figure 3.7) alongside of selectivity as the time passes, also the yield is increasing as the time passes (Figure 3.8).

Table 3.3. Continuous flow reaction of aniline and propylene carbonate with 33 Br/APS/PAI-HFs.

Reaction Time/min	Conversion of Aniline (%)	Selectivity of the product (%)	Yield of Product (%)
5	30.36	97.61	29.63
15	49.76	96.66	48.10
30	51.41	96.32	49.52
60	54.36	97.97	53.26
90	56.34	97.99	55.20
120	60.75	97.84	59.43

Reaction conditions: aniline: 2 mmol, propylene carbonate: 10 mmol, 140 ˚C, 33 Br/APS/PAI-HFs: 0.5 g.

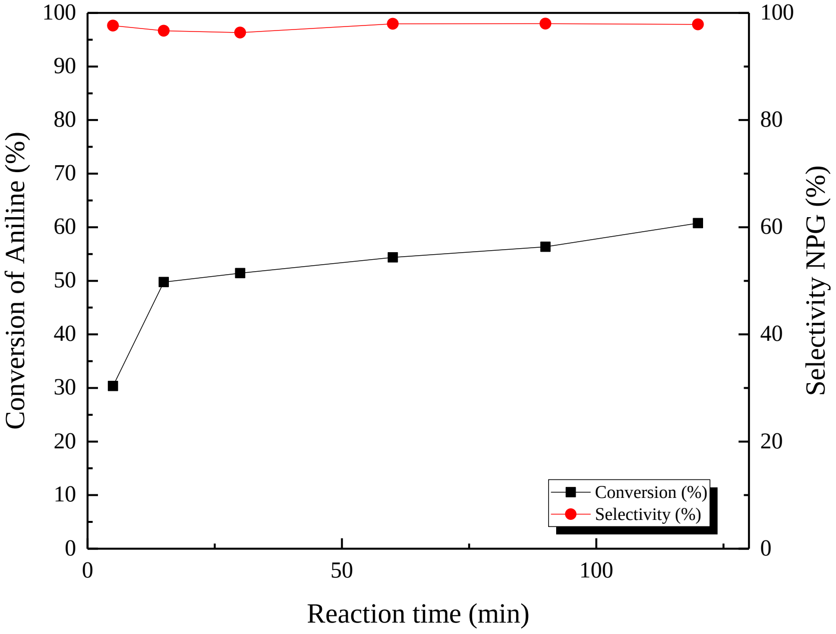


Figure 3.7. Effect of reaction time. Reaction conditions: aniline: 2 mmol, propylene carbonate: 10 mmol, 33 Br/APS/PAI-HFs in continuous flow reactor.

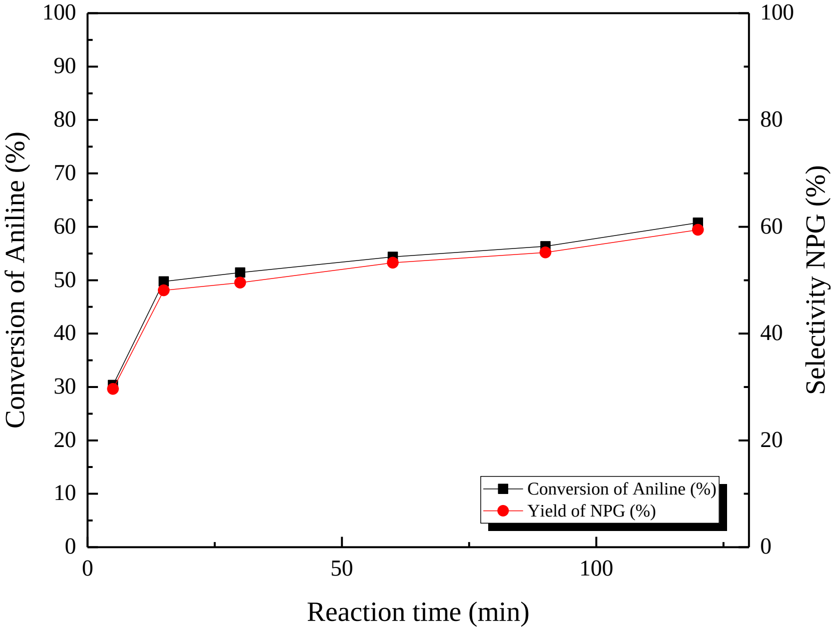


Figure 3.8**.** Effect of reaction time on yield. Reaction conditions: aniline: 2 mmol, propylene carbonate: 10 mmol, 33 Br/APS/PAI-HFs in continuous flow reactor.

3.2. FIBER CHARACTERIZATION

The characterization of the hollow fiber was done of bare hollow fiber PAI-HFs, APS/PAI-HFs, Br/APS/PAI-HFs (before reaction), and Br/APS/PAI-HFs (after reaction) using Solid FTIR and N_2 Physisorption and the data are shown in the tables below that discussed the BET surface area and pore volume.

3.2.1. 28 Br/APS/PAI-HFs Characterizations. It can be noticed that the surface area of the bare 28 PAI-HFs was decreased by approximately 80% when it was grafted with APS and this may be as a result of the crosslinking of the walls of the fiber by the reaction that involves ring opining (Table 3.4). On the contrary, when Br immobilized on the 28 APS/PAI-HFs we noticed an increase of the surface area of the catalyst which may be due to the implementation process of Br using 1,2-dibromopropane on the grafted hollow fiber where the bore volume slightly decreased. The decrease in porosity can be explained by the occupation of 1,2-dibromopropane to the pore sites which is a confirmation to successfully immobilized Br on the hollow fiber. The similarity of the hollow fiber before and after the reaction was confirmed (Figure 3.11). Moreover, N_2 Physisorption was shown in (Figure 3.9) which is according to IUPAC is type IV isotherms.

3.2.2. 33 Br/APS/PAI-HFs Characterizations. From the data collected that the surface area of the bare 33 PAI-HFs was increased by dramatically when it was grafted with APS and this may be as a result of the crosslinking of the walls of the fiber by the reaction that involves ring opining and swelling of APS because it was noticed after grafting PAI-HFs with APS a diameter increase in the fiber.

Table 3.4. Properties of 28 APS/PAI-HFs.

Material	Bare PAI-HFs	APS/PAI-HFs	Br/APS/PAI-HFs (before reaction)	Br/APS/PAI-HFs (after reaction)
S_{BET} (m²/g)	57.54	8.51	22.37	8.56
V_{pore} (cm³/g)	0.25	0.03	0.027	0.026

Surface area: Determined by nitrogen physisorption at 77 K. Total Pore volume: determined by BJH method

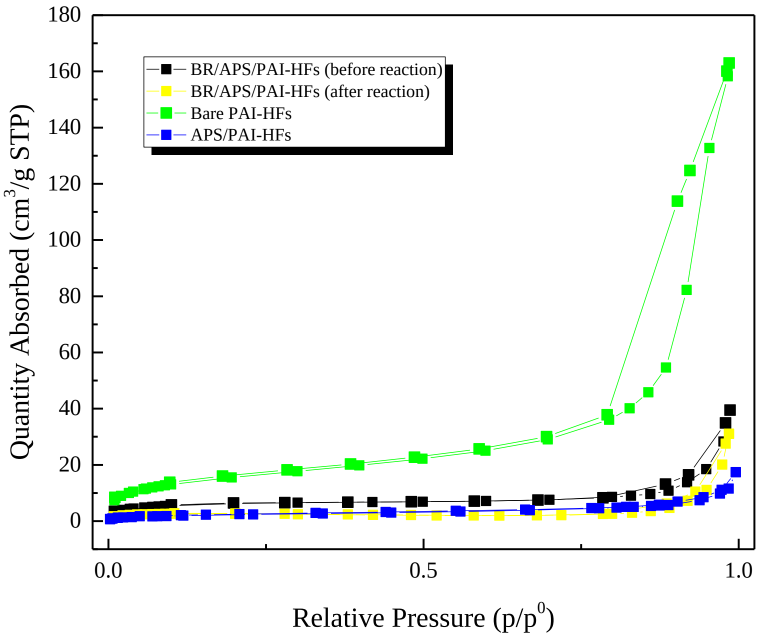


Figure 3.9. Nitrogen adsorption/desorption isotherms at 77 K for 28 Br/APS/PAI-HFs.

On the contrary, when Br immobilized on the 33 APS/PAI-HFs we noticed a 60% decrease of the surface area of the catalyst which may be due to the implementation process of Br using 1, 2-dibromopropane on the grafted hollow fiber where the bore volume slightly decreased (Table 3.5). The decrease in porosity can be explained by the occupation of 1,2-dibromopropane to the pore sites which is a confirmation to successfully immobilized Br on the hollow fiber. The similarity of the hollow fiber before and after the reaction was confirmed (Figure 3.11). Moreover, N_2 Physisorption was shown in (Figure 3.10) which is according to IUPAC is type IV isotherms.

Table 3.5. Properties of 33 APS/PAI-HFs

Material	Bare PAI-HFs	APS/PAI-HFs	Br/APS/PAI-HFs (before reaction)	Br/APS/PAI-HFs (after reaction)
S_{BET} (m^2/g)	40.04	21.03	7.53	6.95
V_{pore} (cm^3/g)	0.16	0.042	0.015	0.015

Surface area: Determined by nitrogen physisorption at 77 K. Total Pore volume: determined by BJH method

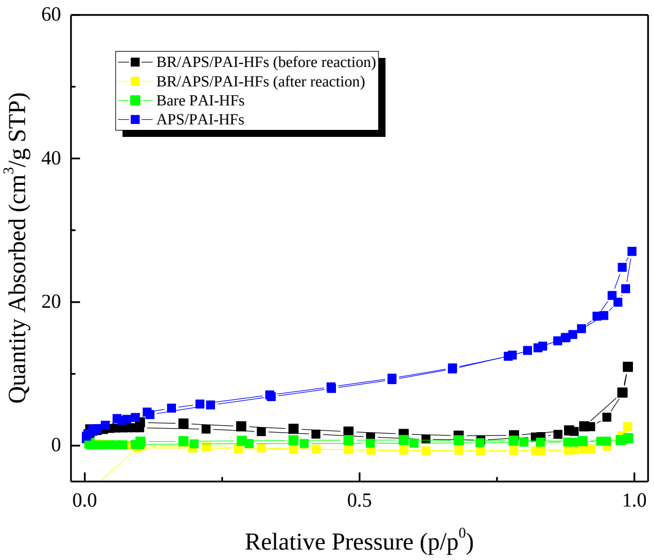


Figure 3.10. Nitrogen adsorption/desorption isotherms at 77 K for 33Br/APS/PAI-HFs

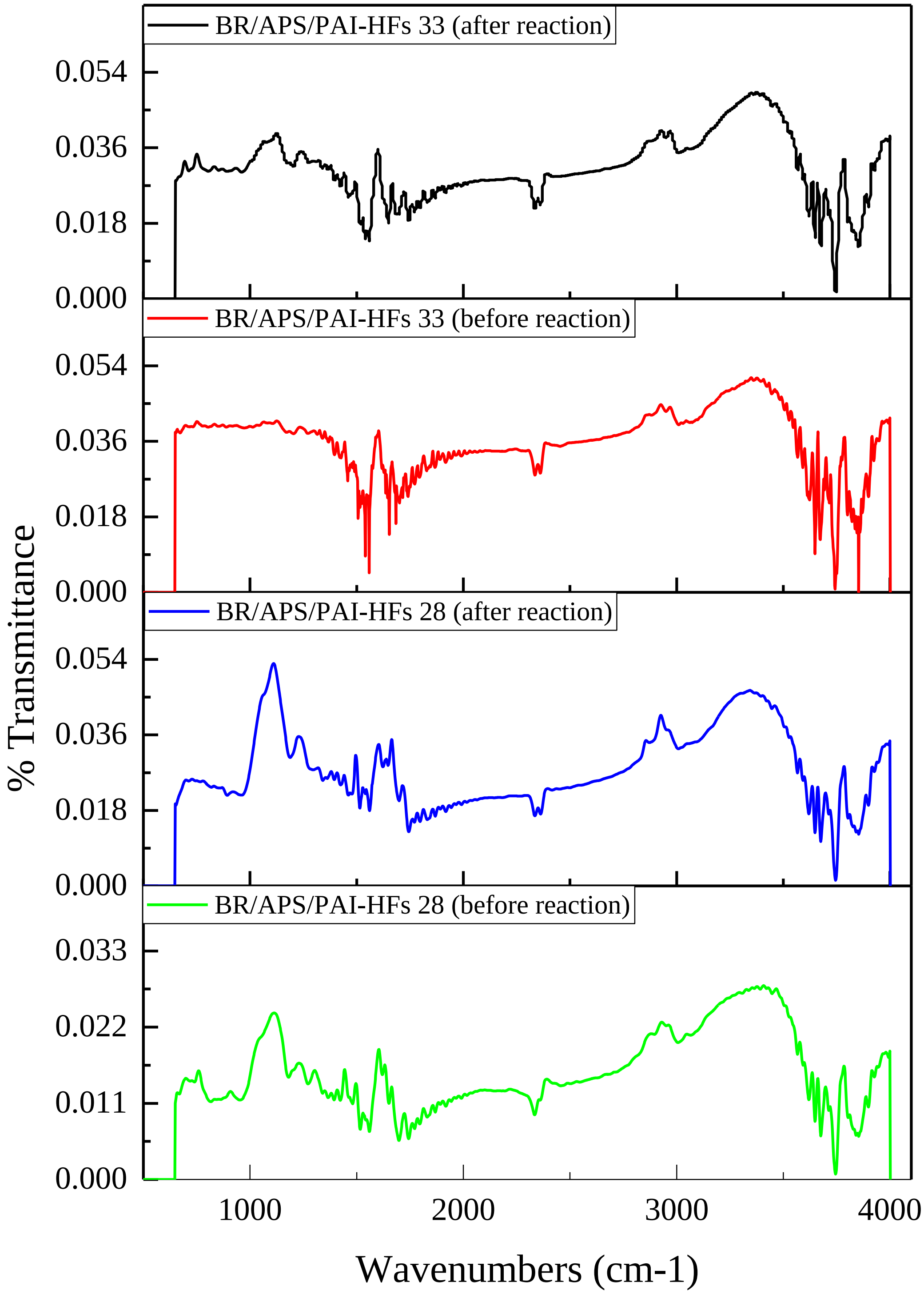


Figure 3.11. FTIR results for both 28,33 Br/APS/PAI-HFs before and after reaction.

4. CONCLUSION

This study is a proof-of-concept study that demonstrate that Br was successfully immobilized permanently into a porous polymeric material hollow fiber (Br/APS/PAI-HFs) and used in various reactions with different types of reactors. This type of catalyst can produce a very innovative system that can be conducted in various applications to express the benefits of nanocatalysts in batch system, packed-pes and continuous reactors. As the results shows that the conversion and selectivity are the highest in the pressurized batch system but when it is compared to the continuous flow reactor, higher numbers of conversion, yield and selectivity can be achieved in shorter time than the batch system. The structure and the properties of the hollow fiber plays a significant role in the reaction providing large surface area compared to volume which is excellent to the mass transfer process and low flow resistance in the continuous flow reactor. The future idea is to scale-up the continuous reaction to be conducted in a real size plant. Also, the ability to test different halogens in this to compare the efficiency of the catalyst using different immobilized substance.

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