

本科毕业论文

Synthesis of Quaternary Ammonium Salts with Different End-capping Structures and Their Application in Molecular Sieve Synthesis

学院名称	化学与化工学院
专业班级	应用化学(国际班)18-1
学生姓名	刘水清
学 号	201894020032
导师姓名	王金桂

2022年5月20日

齐鲁工业大学本科毕业设计(论文)

原创性声明

本人郑重声明:所呈交的毕业设计(论文),是本人在指导教师的指导下 独立研究、撰写的成果。设计(论文)中引用他人的文献、数据、图件、资料, 均已在设计(论文)中加以说明,除此之外,本设计(论文)不含任何其他个人 或集体已经发表或撰写的成果作品。对本文研究做出重要贡献的个人和集体,均 已在文中作了明确说明并表示了谢意。本声明的法律结果由本人承担。

动的济

毕业设计(论文)作者签名:

2022年05月20日

齐鲁工业大学关于毕业设计(论文)

使用授权的说明

本毕业设计(论文)作者完全了解学校有关保留、使用毕业设计(论文)的 规定,即:学校有权保留、送交设计(论文)的复印件,允许设计(论文)被查 阅和借阅,学校可以公布设计(论文)的全部或部分内容,可以采用影印、扫描 等复制手段保存本设计(论文)。

动动床 指导教师签名: 毕业设计(论文)作者签名: 2022年05月20日 2022年05月20日

Contents

ABSTRACT	2
摘 要	2
Chapter 1 Introduction	3
1.1 Primary Introduction	3
1.2 Synthesis of nanosheets zeolites by quaternary ammoniums	3
1.2.1 ZSM-5 Zeolite	3
1.2.2 MFI structure	4
1.2.3 Synthesis of MFI structure by quaternary ammoniums	4
1.3 Nano Materials	7
1.3.1 The Features of Nano Materials	7
1.3.2 The Resent Research Topics of Porous Nanomaterials	8
1.3.3 The Application in life of Nanomaterials	8
1.4 Material characterization methods	11
1.4.1 X-ray powder diffractometer	11
1.4.2 Physical adsorption	11
1.4.3 Inductively coupled plasma optical emission spectrometer	12
1.4.4 Scanning electron microscope	12
1.4.5 Transmission electron microscope	12
1.4.6 Ultraviolet-visible spectrophotometer	12
1.4.7 Infrared spectrometer	13
Chapter 2 Experiment section	14
2.1 Experiment medicine and instrument	14
2.2 Synthesis process	16
2.2.1 Synthetic SDA	16
2.2.2 Synthetic ZSM-5 zeolite	16
2.2.3 Ion exchange	17
Chapter 3. Results and Analysis	18
3.1 Characterization	18
3.2 Catalytic reactions	23
3.3 Applications of Plastic Degradation	23
Chapter 4 Conclusions and Outlook	25
References	26
Acknowledgements	28

Synthesis of Quaternary Ammonium Salts with Different End-capping Structures and Their Application in Molecular Sieve Synthesis

具有不同封端结构的季铵盐分子合成 及其在分子筛合成中的应用

学院名称	化学与化工学院	
专业班级	应用化学(国际班)18-1	_
学生姓名	刘水清	
学 号	201894020032	
导师姓名	王金桂	
专业技术职务	副教授	

ABSTRACT

Zeolite molecular sieves have complex and changeable structures and unique pore systems, which are excellent catalysts and are widely used in petrochemical industry and fine chemicals synthesis. Zeolite Socony Mobil-5 (ZSM-5) zeolite with ordered microporous-mesoporous characteristics, suitable surface acidity, thermal stability and non-carbon deposition have become one of the landmark research hotspots in the controlled synthesis and application of molecular sieves. In the synthesis of this kind of molecular sieves, different double quaternary ammonium surfactants are used as structural directing agents. The special structure of ZSM-5 is not like the cage of A, X and Y zeolites, and its pore is its cavity, which makes ZSM-5 show unique application potential in adsorption and catalytic applications. In this paper, Quaternary Ammonium Salts with Different End-capping Structures are used as the Structure-directing Agent(SDA), using experimental characterization data for comparative analysis, and the SDA synthesis and its application in Molecular Sieve Synthesis.

Key words: SDA; Molecular Sieve; ZSM-5 zeolite; quaternary ammonium;

摘要

沸石分子筛具有复杂多变的结构和独特的孔道体系,是一种性能优良的催化剂,在石油化工和精细化学品合成领域被广泛应用。Zeolite Socony Mobil - 5 (ZSM-5)型分子筛具有有序的微孔-介孔特征、适宜的表面酸性,热稳定性和不易积碳的特性,已成为分子筛控制合成及其应用研究中标志性的研究热点之一。该类分子筛在合成中采用不同双头季铵盐表面活性剂作结构导向剂,所得具有特殊的结构没有 A 型、X 型和 Y 型沸石那样的笼,其孔道就是它的空腔,使得 ZSM-5 在吸附、催化应用等多方面展现出独特的应用潜力。本文采用不同封端结构的季铵盐作为结构导向剂(SDA),利用实验表征数据进行对比分析,并对 SDA 的合成及其在分子筛合成中的应用进行了研究。

关键词: SDA; 分子筛; ZSM-5 分子筛; 季铵盐;

Chapter 1 Introduction

1.1 Primary Introduction

The artificial synthesis of molecular sieves (zeolite molecular sieves) has been developed for more than half a century. Up to now, there are more than 200 types of molecular sieves with different topologies have been confirmed, and new molecular sieve structures are emerging every year. ^[1] However, the pores of most microporous molecular sieves are less than 1 nm, resulting in the difficulty of molecular transmission. For the reaction catalysts involving macromolecules, it is easy to deactivate due to the blockage of pores due to surface area carbon or coking, thus limiting its application.

1.2 Synthesis of nanosheets zeolites by quaternary ammoniums

Organic ammonium (amine) plays an important structural guiding role in the synthesis of zeolite molecular sieves. For example, the molecular structure of quaternary ammonium surfactants is crucial for the skeleton structure and mesoporous formation of molecular sieves. The application of quaternary ammonium surfactants with different structural types in the synthesis of molecular sieves can synthesize nanocrystalline assembled molecular sieves with multistage pores in one step. Due to the different number of cationic active groups and different molecular sieve frameworks are synthesized. However, the grain morphology of molecular sieves with the same topological structure is also quite different, such as nano-thin layer, nano-needle and nano-rod, which affect the pore structure properties of molecular sieves.

1.2.1 ZSM-5 Zeolite

ZSM-5 zeolite contains ten-membered rings, and its basic structural unit consists of eight five-membered rings. Its crystal structure belongs to the tetragonal system, space group Pnma, lattice constant a=20.1 Å, b=19.9 Å, c=13.4 Å. It has a special structure with no cage like zeolite A, X and Y, and its pore is its cavity. The skeleton is composed of two cross-channel systems, the straight channel is oval, the long axis is $5.7 \sim 5.8$ Å, the short axis is $5.1 \sim 5.2$ Å; the other is a 'Z'-shaped transverse channel with a section close to circular and a pore size of 5.4 ± 0.2 Å. It belongs to mesoporous zeolite. The angle of the zigzag channel is 110 degrees. Sodium ions are located on the symmetric

surface of the ten-membered ring. The anion skeleton density is about $1.79 \text{ g} / \text{cm}^3$. So, the crystal structure of ZSM-5 zeolite is very stable.

ZSM-5 zeolite was synthesized by Mobile Oil Company of the United States in the late 1960s, which is a new zeolite molecular sieve containing organic amine cations. Because of its unique chemical composition, crystal structure and physical and chemical properties, it has shown excellent catalytic performance in many organic catalytic reactions. It has been widely used in industry and has become a promising new catalyst for petrochemical industry.

1.2.2 MFI structure

The MFI structure is described as a combination of two interconnected channel systems. The silicate framework forms sinusoidal 10-member-rings (MR) channels along the direction of the a-axis, interconnected with 10-MR straight channels that run down the b-axis. A tortuous pore path is present along the c-axis. The MFI framework model can be built by connecting pentasil silicate chains.^[2]

Researchers generally believe that the preparation of microporous-mesoporous zeolite molecular sieves is an important way to solve the problem of molecular sieve diffusion. The design and synthesis of such hierarchical molecular sieves has been a hot topic for molecular sieve chemistry researchers. Among many molecular sieves, MFI molecular sieves have been recognized as the most ideal catalysts due to their regular pore size distribution, three-dimensional cross-pore system, high hydrothermal stability, and wide range of adjustable acid properties, which make them exhibit high catalytic activity, selectivity and catalytic life in many petrochemical processes.

Since the first decade of this century, the research on the synthesis of molecular sieves represented by MFI molecular sieves has made a breakthrough. Ryoo and his colleges have synthesized MFI molecular sieves with special morphology, i.e. ZSM-5 nanosheets with nano-thin layer structure. The growth of MFI molecular sieves in the b-axis direction was limited by the guidance of long-chain Gemini quaternary ammonium surfactants, and the MFI molecular sieve structure with nearly single molecular layer thickness was obtained.^[3]

1.2.3 Synthesis of MFI structure by quaternary ammoniums

Various types of quaternary ammonium salts can be used as structural directing agents

(SDA, structure-directing-agent) to synthesize MFI molecular sieves, and the molecular structure is shown in Table 1. Ryoo et al. synthesized MFI nanosheets with a thickness of only 2.0 nm by dynamic crystallization with C22-6-6 surfactant as the structure-directing agent. Schwieger et al. studied the crystallization of the synthesis system of C22-6-6-oriented nano-thin molecular sieve under static conditions and investigated the influence of initial sol composition on the static synthesis of nano-thin molecular sieve from four aspects: silicon-aluminum ratio, alkalinity (OH⁻ / SiO₂), molar ratio of template and crystallization time. The results show that SDA / SiO2 should be within 0.5 - 1 in order to obtain pure-phase nano-thin molecular sieves, and the appropriate OH⁻ / SiO₂ for the synthesis of molecular sieves with different Si / Al ratios is also different. The type of anion matching with ammonium cations in surfactants also has a certain influence on the morphology and growth of molecular sieves. Ryoo et al. first synthesized nano-thin molecular sieves found that OH-type surfactants obtained disordered nano-thin molecular sieves (unilamellar), while Br-type surfactants obtained ordered multilamellar structure (Figure 1). However, subsequent studies found that when Br-type surfactant was used, disordered MFI nano-thin molecular sieves were also obtained by adjusting pH value, which may be due to the change of alkalinity of the system. The results are consistent with the synthesis system of quaternary ammonium salt structure directing agent with long alkyl chain in the range of $C_{22}H_{45}$ - ~ $C_{12}H_{25}$ -, indicating that the molecular sieve and synthesis growth are not controlled by single factor.

diquaternary ammonium	abbreviation	ref
$C_m H_{2m+1} - N^+ (Me)_2 - C_6 H_{12} - N^+ (Me)_2 - C_6 H_{13}$	m = 6 C ₆₋₆₋₆	13
	$m = 8$ C_{8-6-6}	13
	m = 10 C ₁₀₋₆₋₆	13
	m = 12 C ₁₂₋₆₋₆	13
	m = 16 C ₁₆₋₆₋₆	10
	m = 18 C ₁₈₋₆₋₆	9,10
	$m = 20$ C_{20-6-6}	10
	m = 22 C ₂₂₋₆₋₆	6,7
$C_{22}H_{45}$ —N ⁺ (Me) ₂ — C_iH_{2i} —N ⁺ (Me) ₂ — C_6H_{13}	i = 3 C ₂₂₋₃₋₆	11
	i = 6 C ₂₂₋₆₋₆	6,7
	i = 8 C ₂₂₋₈₋₆	11
$C_{e}H_{2n+1}$ - N ⁺ (Me) 2 - $C_{e}H_{12}$ - N ⁺ (Me) 2 - $C_{3}H_{7}$	$n = 3$ C_{22-3-6}	11
·n 2n+1 · · · · 2 · 0 12 · · · · 2 · 5 /	n = 6 C ₂₂₋₆₋₆	6,7
$C_{22}H_{45}$ —N ⁺ (Me) ₂ — $C_{6}H_{12}$ —N ⁺ (Me) ₂ — $C_{i}H_{2i+1}$	j = 0 C ₂₂₋₆	10, 11
	j = 3 C ₂₂₋₆₋₃	10
	j = 8 C ₂₂₋₆₋₈	10, 11
$C_{18}H_{37}$ —N ⁺ (Me) 2— $C_{6}H_{12}$ —N ⁺ (R) 2— $C_{6}H_{13}$	$R:Me = C_{18-6}N_2 (Me_2)$	11
	R: Et $C_{18-6}N_2(Et_2)$	11
	R: Pr $C_{18-6}N_2(Pr_2)$	11
	R: Bu $C_{18-6}N_2$ (Bu ₂)	11
$C_{18}H_{37}$ —N ⁺ (Me) ₂ — $C_{6}H_{12}$ —N ⁺ (Pr) ₂ —Pr	$C_{18-6}N_2$ (Pr ₃)	11

Table 1. Di-quaternary ammonium surfactants as SDA for MFI zeolite



Figure 1. Crystallization model of MFI nanosheets.^[6]

The experiment mentioned in this paper used bromoadamantane SDA and bromocyclohexane SDA as structural directing agents to synthesize a series of nano-thin molecular sieves with high Si / Al ratio. The relationship between Si / Al ratio and crystallization temperature, template dosage was obtained, and the pore properties of molecular sieves with different Si / Al ratio were studied. Compared with the study of Ryoo et al., this experiment optimized the suitable synthesis conditions for the static synthesis of nano-thin MFI zeolite by C₁₈₋₆₋₆, reduced the relative amount of template (n $(SDA) / n (SiO_2) = 0.08 - 0.12$, and simplified the synthesis method of template. ZSM-5 molecular sieve with the actual molar ratio of Si to Al of 100 was synthesized, so as to realize the adjustment of the acidity of the thin layer molecular sieve. At the same time, with the increase of Si / Al ratio, the specific surface area, mesoporous surface area and mesoporous volume of zeolite increase, while the micropore surface area and micropore volume decrease. The synthesis phase diagram of nano-thin ZSM-5 molecular sieve was determined by studying the influence of synthesis chemistry and synthesis parameters of nano-thin ZSM-5 molecular sieve. This study not only greatly reduced the amount of template agent and crystallization time, but also laid the foundation for the preparation of nano-thin ZSM-5 molecular sieves with different Si / Al ratios and broadening their application scope, providing a research foundation for the morphology control synthesis of other molecular sieves. In order to study the effect of

molecular structure groups of diquaternary ammonium salt surfactants on the growth of molecular sieves, Ryoo et al. synthesized two kinds of surfactants on the basis of C₂₂₋₆Br₂ compounds, one is diquaternary ammonium salt which shortens the length of long chain alkyl C₂₂-chain, the other is quaternary ammonium salt which changes the side of short chain alkyl C₆. The results showed that : 1) With C₂₂₋₆₋₆Br₂ \sim C₂₀₋₆₋₆Br₂ \sim C₁₂₋₆₋₃Br₂ as SDA synthetic molecular sieve, compared with X-ray diffraction patterns, with the shortening of hydrophobic chain, the first-order reflection peak of small angle range shifted to larger 2 θ value, and the relative diffraction peak intensity of small angle range decreased ; 2) Similar multilayer molecular sieves can also be synthesized by using C₂₂₋₆₋₀, C₂₂₋₆₋₃, and C₂₂₋₆₋₈ as SDA, but the different structures of these SDA also affect the crystallization time required for molecular sieve synthesis and the orderliness of thin layer stacking of molecular sieves. The product with C₂₂₋₆₋₆Br₂ as SDA has the best structural order and the shortest synthesis time. 3) Comparison showed that the short side chain of C₆H₁₃ - alkyl as surfactant provided the best group spacing for the formation of nano-thin layer.

1.3 Nano Materials 1.3.1 The Features of Nano Materials

When it comes to nanomaterials, we usually refer to materials composed of basic units with a size of 1-100nm. Nano materials has gradually been used in various fields in life and scientific research. Precisely because its size is between 1-100nm, which is close to the wavelength of light, nanomaterials can show different characteristics from other traditional materials under the same conditions. Nanomaterials are in the transition limit between atomic clusters and macroscopic objects. Nanomaterials have Surface effect, Small size effect and Macroscopic quantum tunneling effect. When people divide the macro-object into ultrafine particles (nanoscale), it will show many strange characteristics, such as its optical, thermal, electrical, magnetic, mechanical and chemical properties can be significantly different from those of normal sized material solids.

The reason why nanoparticles are different from normal materials is that the surface area of nanoparticles increases relatively, nanomaterials have a large surface area, the surface of ultrafine particles is full of ladder-like structures, which represent unstable atoms with high surface energy. These atoms are easy to bond with single atoms, and

- 7 -

provide large surface for the active atoms due to the reduction of particle size, the above can make them a good carrier for metal atoms. Nanoporous materials are composed of regular organic or inorganic frameworks that support regular porous structures. Most nanoporous materials can be divided into bulk materials or thin films. This makes it an ideal structure of catalyst materials and has always been a research hotspot.

1.3.2 The Resent Research Topics of Porous Nanomaterials

In recent years, the synthesis, characterization and application of inorganic and organic porous nanomaterials are discussed, including magnetic mesoporous silica adsorption of copper ions in water,^[4] recyclable magnetic core-shell structured nitrite fluorescent sensing nanomaterials, ^[5] rhodamine molecular functionalized core-shell structured nanomaterials for nitrite optical sensing, ^[6] rhodamine derivative modified MOF colorimetric fluorescence sensing response to anthrax biomarkers, ^[7] mesoporous silica / polypyrrole nanomaterials modified microbial fuel cell anode, ^[8] magnetic core-shell Fe3O4 @ MCM-41 / multi-walled carbon nanotube composite modified microbial fuel cell anode performance, ^[9] Fe3O4 @ SiO2 / multi-walled carbon nanotube / polypyrrole modified anode microbial fuel cell-constructed wetland system.^{[10][11]}

1.3.3 The Application in life of Nanomaterials1. Antibacterial agents in biomedicine

Microbial infection is one of the problems scientists are trying to overcome today. The arrival of antibiotics has given people hope, but the subsequent drug resistance limits the use of antibiotics. Due to the excellent properties of nanomaterials, some researchers have focused on nanomaterials. In recent years, the antibacterial properties of nanomaterials have been applied. Compared with antibiotics, antibacterial nanoparticles have the advantages of low toxicity, overcoming drug resistance and low cost. The recognized antibacterial mechanisms include sharp edge-mediated cleavage, oxidative stress and cell retention. Various nanomaterials such as graphene, Ag, Ag2O, TiO2, ZnO and CuO have been used as antibacterial agents.^[12]

Some scholars have pointed out that biomimetic calcium phosphate mineralization-GO / chitosan (OCP-GO / CS) scaffold is expected to become an ideal material for bone tissue engineering. The scaffold can not only promote the proliferation

- 8 -

and differentiation of bone marrow stromal cells, induce bone tissue regeneration, but also effectively inhibit the growth of Staphylococcus aureus and Escherichia coli, and has good biocompatibility. ZnO / GO-COOH composites have also been proved to have antibacterial effect against Streptococcus mutans and have obvious osteogenic effect.

Prof. Le Huirong, the chief researcher of the Future Laboratory of Tsinghua University, collaborated with Prof.R. Handy, a famous nano virologist at the School of Biology, University of Plymouth, UK, to produce TiO2 nanoporous structure on the surface of titanium alloy and inlay a variety of nanoparticles. For example, anti-microbial nanoparticles such as Ag and ZnO were implanted by sol-gel method, which improved the anti-microbial properties of dental and orthopedic materials at the early stage of implantation.^[13]

2. Decomposition and pollution reduction in the field of energy and environmental protection

At present, with the rapid development of global economy and industry, the environmental pollution caused by toxic or refractory organic compounds is becoming increasingly serious, which has become one of the problems that cannot be ignored all over the world. Studies have shown that two different semiconductor nanomaterials, are similar to semiconductor p-n junction, which can greatly improve the absorption capacity of visible light and accelerate the cracking of organic dyes.

For example, NiO is a p-type semiconductor material, CdS is n-type semiconductor. CdS nanoparticles adhere to the surface of NiO crystal plate, resulting in changes in the band structure, resulting in more free electrons on the CdS surface and more electron holes on the NiO surface. The material is powdered into dye wastewater containing Congo red, which can greatly improve the decomposition efficiency of organic pollutants under visible light irradiation.^[14]

Nanoscale two-dimensional materials, such as graphene oxide, MoS2 and WS2, can enhance the photocatalytic performance of the surface, which was initially applied to the solar hydrolysis hydrogen production technology. MoS2 nanoparticles were deposited on graphene oxide sheets by hydrothermal method by Dr. H. Dai of Stanford University,^[15] showing excellent photocatalytic performance in the process of hydrogen production, which is related to the edge effect of MoS2 nanosheets and the good conductivity of graphene. The J. H. He team of National University of Taiwan ^[16]

deposited monolayer MoS2 film on p-type silicon wafer, which improved the absorption efficiency of solar energy and converted the energy conversion density to 20 mA/cm2. In addition, ZnO-TiO2composite coating has excellent light absorption and catalytic effect and has been widely concerned in the field of solar energy conversion and water to hydrogen.

3. Upgrading in the field of aerospace

With the development of nanomaterial preparation technology and the acceleration of industrialization, many scholars in China and abroad have carried out a lot of research on its application in aerospace, energy and other fields. Nano-carbon composites can keep the excellent properties of nano-carbon at the macro scale, give full play to the synergistic effect of composite materials and nanotechnology. Its lightweight and multi-functional characteristics can meet the lightweight needs of aerospace field and inject new vitality into the development of aerospace materials. ^[17]

The research of Kumar Group of Georgia Institute of Technology in the United States showed that the tensile strength of carbon fibers produced by carbonization of frozen rubber spinning single-walled carbon nanotubes / polyacrylonitrile nanocomposites was 50 % higher than that of carbon fibers prepared by polyacrylonitrile, which was mainly attributed to the high arrangement of nanotubes in polyacrylonitrile fibers. In addition to increasing the tensile strength of the material, the addition of carbon nanotubes in the composite can also reduce the thermal expansion coefficient of the material and reduce the deformation of the material caused by high and low temperatures, which is very suitable for satellite antennas with high precision pointing requirements.

Peng et al ^[18] proposed and realized the concept of graphene nanobelt sponge structure based on the idea of cross-scale and bionic design, obtained graphene nanobelt sponge and realized the composite, so that the tensile strength (increased by 4 times), modulus (increased by 4 times) and toughness (increased by 10 times) of the composite were improved at the same time. At the same time, inspired by the ' drug dispersion in water ' technology, the graphene porous skeleton composite technology is proposed to solve the problem that nano-carbon materials are difficult to disperse in the resin matrix, and the technology is introduced into the carbon fiber composites, which improves the shear and compression properties of carbon fiber composites. The results are reported on the first page website of China Academy of Launch Vehicle Technology.

1.4 Material characterization methods 1.4.1 X-ray powder diffractometer

In 1912, Laue et al., based on theoretical predictions, confirmed that atoms in crystalline materials with a distance of tens to hundreds of picometers (pm) are periodically arranged; this periodically arranged atomic structure can become a "diffraction grating" for X-ray diffraction. "; X-rays have wave characteristics, are electromagnetic waves with wavelengths of tens to hundreds of picometers and have the ability to diffract. ^[19] This experiment became the first milestone in X-ray diffraction. When a monochromatic X-ray is incident on a crystal, since the crystal is composed of a unit cell with atoms regularly arranged, the distance between these regularly arranged atoms has the same order of magnitude as the wavelength of the incident X-ray in X-ray diffraction analysis, so it is scattered by different atoms. The X-rays interfere with each other, resulting in strong X-ray diffraction in some special directions. The orientation and intensity of the diffraction lines in space are closely related to the crystal structure. The diffraction pattern produced by each crystal reflects the atoms inside the crystal. distribution law. This is the basic principle of X-ray diffraction.

1.4.2 Physical adsorption

Brunauer–Emmett–Teller (BET) theory aims to explain the physical adsorption of gas molecules on a solid surface and serves as the basis for a meaningful analysis technique for the measurement of the specific surface area of materials. The observations are very often referred to as physical adsorption or physisorption. In 1938, Stephen Brunauer, Paul Hugh Emmett, and Edward Teller presented their theory.^[20] BET theory applies to systems of multilayer adsorption that usually utilize a probing gas (called the adsorbate) that does not react chemically with the adsorptive (the material upon which the gas attaches to and the gas phase is called the adsorptive) to quantify specific surface area. Nitrogen is the most commonly employed gaseous adsorbate for probing surface(s). For this reason, standard BET analysis is most often conducted at the boiling temperature of N2 (77 K). Other probing adsorbates are also utilized, albeit less frequently, allowing the measurement of surface area at different temperatures and measurement scales. These include argon, carbon dioxide, and water. Specific surface area definable. Thus quantities of a specific surface area determined through BET theory may depend

Graduation Design (Thesis) of the 22nd Undergraduate Course of Qilu University of Technology

on the adsorbate molecule utilized and its adsorption cross-section.^[21]

1.4.3 Inductively coupled plasma optical emission spectrometer

Inductively coupled plasma atomic emission spectroscopy (ICP-AES), also referred to inductively coupled plasma optical emission spectrometry (ICP-OES), is an analytical technique used for detecting different elements. It is a type of emission spectroscopy that uses the inductively coupled plasma to produce excited atoms and ions that emit electromagnetic radiation at certain wavelengths characteristic of a particular element. The plasma is a high-temperature source of an ionized source gas (often argon). The plasma is sustained and maintained by inductive coupling from cooled electrical coils at megahertz frequencies. The source temperature is in the range of 6000 to 10,000 K. The intensity of the emissions from various wavelengths of light are proportional to the concentrations of the elements within the sample.

1.4.4 Scanning electron microscope

A scanning electron microscope (SEM) is a type of electron microscope that processes images of a sample by scanning the surface with a focused beam of electrons. The electrons interact with atoms on the surface of the sample, producing various signals that contain information about the surface topography and composition of the sample.

1.4.5 Transmission electron microscope

Transmission electron microscopy (TEM) is a microscopy technique in which a beam of electrons is transmitted through a specimen to form an image. The specimen is normally an ultrathin section less than 100 nm thick or a suspension on a grid. An image is formed from the interaction of the electrons with the sample as the beam is transmitted through the specimen.

1.4.6 Ultraviolet-visible spectrophotometer

In 1852, Beer referred to articles published by Bouguer in 1729 and Lambert in 1760, and proposed the fundamental law of spectrophotometry, when the thickness of the liquid layer is equal, the strength of the color is proportional to the concentration of the solution itself, thus laying the theoretical foundation of spectrophotometry, which is the

- 12 -

famous so-called Lambert Beer's law.

It is usually caused by the transition of valence electrons after molecules or ions absorb ultraviolet or visible light. By observing the maximum absorption peak position of the ultraviolet-visible spectrum, the characteristic absorption of the compound in the ultraviolet-visible spectrum can be identified.

The diffuse reflectance UV-vis spectra (DRUV / vis) were measured at 298 K using barium sulfate as reference at Shimadzu UV-2450 spectrophotometer.

1.4.7 Infrared spectrometer

The Fourier transform infrared transmission spectrum (FTIR) is a technique which is used to obtain infrared spectrum of absorption, emission, and photoconductivity of solid, liquid, and gas. It is used to detect different functional groups in PHB. FTIR spectrum is recorded between 4000 and 400 cm⁻¹.

Reagent	Specifications	Manufacturer		
Ethanol	AR	Sinopharm Chemical Reagent Co., Ltd		
Ethyl ether	AR	Sinopharm Chemical Reagent Co., Ltd		
Acetonitrile	AR	Sinopharm Chemical Reagent Co., Ltd		
Sodium hydroxide	AR	Sinopharm Chemical Reagent Co., Ltd		
Sulfuric acid	AR	Sinopharm Chemical Reagent Co., Ltd		
Aluminium sulfate	AR	Sinopharm Chemical Reagent Co., Ltd		
Ammonium sulfate	AR	Sinopharm Chemical Reagent Co., Ltd		
Titanium butoxide (TBOT)	AR	Macklin Biochemical Co., Ltd		
Ethyl acetate	AR	Macklin Biochemical Co., Ltd		
Tetraethyl orthosilicate (TEOS)	98%	Macklin Biochemical Co., Ltd		
N, N, N, N-tetramethyl-				
1,6-hexanediamine	AR	Macklin Biochemical Co., Ltd		
1,6-dibromohexane	AR	Macklin Biochemical Co., Ltd		
1-bromohexane	AR	Macklin Biochemical Co., Ltd		
4-vinylbenzyl chloride	90%, stabilized with	TBC+2-Nitro-p-cresol		
		Macklin Biochemical Co., Ltd		
Dichloromethane	AR	Fuyu Chemical Co., Ltd		
7-Bromo-1-heptene	AR	Aladdin Technology Co., Ltd		
11-Bromo-1-undecene	AR	Aladdin Technology Co., Ltd		
Toluene	AR	Yantai Yuandong Fine Chem. Co.,Ltd		
ZSM-5	Si/Al=50	Nankai University		
(Bromomethyl)cyclohexane	AR	Tongchuang Chemical Co., Ltd		
Hydrogen peroxide	AR	Tianjin Kemiou Chemical Reagent Co.,		

Chapter 2 Experiment section

Graduation Design (Thesis) of the 22nd Undergraduate Course of Qilu University of Technology

Instrument	Type	Manufacturer			
Intelligent magnetic agitator	ZnCl-BS140*140	Gongyi Yuhua Instrument Co., Ltd			
Electronic balance	QUINTIX224-1CN	Sartorius			
Vacuum drying oven Ltd	DZF-6216	Shanghai Yiheng Scientific Instrument Co.,			
Two-value capacitor					
asynchronous motor	YL71240	Shaoxing Wanpeng Electromechanical Co., Ltd			
UV-visible spectrophotometer	UV2800S	Shanghai Sunny Hengping Scientific Instrument Co., Ltd.			
Fluorescence					
Spectrophotometer	F97pro	Lengguang Technology			
Ultrasonic signal					
generator/ultrasonic probe	Joyn-1000D	Shanghai Joyn Electronic CO., Ltd			
Heat-collecting thermostatic magnetic stirrer Factory	DF-101S	Gongyi Yingyu High- tech Instrument			
Laser particle size analyzer	Mastersize 2000	Malvern			

2.2 Synthesis process 2.2.1 Synthetic SDA

52 ml N, N, N, N, N-tetramethyl-1,6-hexanediamine (0.25 mol) was added into 200 ml ethanol in a three-necked flask, and then 5 ml 1-bromohexane (0.035 mol) was added. The reaction was refluxed in oil bath at 70 °C for 12h. After the reaction was done and cooled, the ethanol solution was removed by rotary evaporation, and the remaining reaction solution was separated by separating funnel. After clear the stratification, two layers are formed, the upper layer was N, N, N, N-tetramethyl-1,6-hexanediamine, this part was not reacted and can be recycled. The bottom layer was the reaction product, which was washed with ether after stratification and dried in vacuum at 40 °C to obtain the first step product $[C_6H_{13}-N(CH_3)_2-C_6H_{13}-N(CH_3)_2-Br]$.

Took the first step product $[C_6H_{13}-N(CH_3)_2-C_6H_{13}-N(CH_3)_2-Br]$ 5.0g (15mmol), adding 1-bromoadamantane and 1-(Bromomethyl)cyclohexene 2.15g and 1.75g (10mmol) into two different flasks, adding 50ml acetonitrile and 50ml toluene to each, remain the reaction conditions at 70 °C for 12h. When the reaction was finished, rotary evaporation to remove the solvent, adding a large number of ethyl acetate to precipitate the products, vacuum filtration, washed by ethyl acetate, 40 °C vacuum drying for 24h.

The structural formula of the product reacted from 1-bromoadamantane can be marked as $C_{10}H_{15}-N^+(Me)_2-C_6H_{12}-N^+(Me)_2-C_6H_{13}(Br_2)$, briefly $C_{Adh-6-6}$ Br₂.

The structural formula of the product reacted from 1-(Bromomethyl)cyclohexene can be marked as C_7H_{13} - N⁺(Me)₂-C₆H₁₂-N⁺(Me)₂-C₆H₁₃(Br₂), briefly C_{Bmc-6-6} Br₂.

2.2.2 Synthetic ZSM-5 zeolite

Ethyl orthosilicate was added into the mixture of SDA, sodium hydroxide, sulfuric acid and water. After stirring for 2h, aluminum sulfate was added and stirring for 10 min. The molar ratio of each substance in the obtained mixture was $SiO2 : Na2O : Al_2O_3 : SDA : H_2SO_4 : H_2O = 100 : 20 : 1 : 10 : 18 : 4000$. The mixture was transferred to a stainless-steel reactor with PTFE liner and crystallized in a homogeneous reactor at 150 °C and 60r/min for 7 days. The obtained samples were centrifuged and washed by water for three times, dried in vacuum at 80 °C, and then calcined in a muffle furnace at 550 °C for 6h to obtain ZSM-5 zeolite, samples were labeled ZSM-5-SDA (such as ZSM-5-1-bromoadamantane and ZSM-5-1-(bromomethyl)cyclohexene).

2.2.3 Ion exchange

The calcined molecular sieves were added into 1mol / L ammonium sulfate solution according to the mass ratio of 1 : 50, under the condition of 80 °C oil bath, condensed and refluxed in three-neck flask for 4h, repeated twice, centrifuged and washed three times, put into 80 °C oven vacuum drying, calcined at 550 °C for 6h, the final sample was obtained and was labeled HZSM-5-bromoadamantane and HZSM-5-(Bromomethyl)cyclohexene.

Chapter 3. Results and Analysis

Characterization and analysis of the synthesized SDA-bromoadamantane and SDA-(Bromomethyl)cyclohexene.

The synthesis step diagram is as follows:



Figure 2. Synthesis of end-capping SDA-bromoadamantane.



Figure 3. Synthesis of end-capping SDA-(Bromomethyl)cyclohexene.

3.1 Characterization

Powder X-ray diffraction (XRD) was carried out using a Bruker Powder D8 Advance diffractometer operated at 40 kV and 40 mA with CuK α radiation (λ =1.5418 Angstrom). Nitrogen adsorption-desorption isotherms were measured on a TrisStar II 3020 sorption analyzer at 77 K.The samples were firstly degassed at 573 K under vacuum condition for 10 hours before testing. Elemental analyses (Al and Si) were measured on an inductively coupled plasma optical emission spectrometer (Perkin Elmer ICP Optima 2000DV). Field-emission scanning electron microscope (SEM) images were recorded on a Hitachi Regulus8220 microscope at 5 kV. Transmission electron microscopy (TEM) images were obtained using a JEOL JEM-1400 TEM microscope working at 100 kV. Diffuse reflectance ultraviolet-visible (DRUV-vis) spectra were measured on a Shimadzu UV-2450 spectrophotometer at 298 K with BaSO4 as a reference. The Fourier transform infrared transmission spectra (FTIR) were measured on a Shimadzu IRPrestige-21 spectrometer as KBr pellets.



Figure 4. PXRD Patterns of Zeolites Prepared by Different SDA.

The XRD (Figure 4.) showed ZSM-5- bromoadamantane and ZSM-5-(Bromomethyl)cyclohexene samples possessed the characteristic diffraction peaks of MFI (a zeolite framework code by International Zeolite Association) topology. The PXRD pattern of the achieved solid when the Si/Al molar ratio was fixed at 100, shows the presence of very low-intense and broad peaks, which suggest the crystallization of this material as tiny crystallites (see Figure 5a). The homogeneous crystallization of the sample and its nanocrystalline nature have been studied by scanning and transmission electron microscopy(SEM and TEM).

Graduation Design (Thesis) of the 22nd Undergraduate Course of Qilu University of Technology



Figure 5. SEM and TEM images of the calcined ZSM-5 product. (a,b)ZSM-5bromoadamantane and (c,d)ZSM-5-(Bromomethyl)cyclohexene.

SEM and TEM images (Fig. 5) showed that the synthesized ZSM-5bromoadamantane zeolites have a crystal size about 0.8-1.0um, and the size of the ZSM-5-(Bromomethyl)cyclohexene is about 0.5um, and all have formed Micropore-level pore structure, and the formation of hierarchical pores, the MFI structure can be seen as well.



Figure 6. NMR Spectroscopy and Structural Formula of end-capping SDA-bromoadamantane.



Figure 7. NMR Spectroscopy and Structural Formula of end-capping SDA-(Bromomethyl)cyclohexene.

The structure of the SDA(s) are analyzed by NMR spectroscopy, which can be ensured that the ZSM-5 zeolites synthesized later has a certain degree of purity. It can be known from the NMR spectrum that the sample obtained are end-capping SDA-bromoadamantane and end-capping SDA-(Bromomethyl)cyclohexene. Other Graduation Design (Thesis) of the 22nd Undergraduate Course of Qilu University of Technology

unmarked peaks may be impurity peaks, which do not have to do extra analysis.



Figure 8. Nitrogen adsorption/desorption isotherms of ZSM-5-bromoadamantane and ZSM-5-(bromomethyl)cyclohexene.



Figure 10. Pore Radius of ZSM-5-bromoadamantane and ZSM-5-(bromomethyl)cyclohexene.

	Specific	Total pore	Micropore
	surface area	volume	volume
	$(m^2 \cdot g^{-1})$	$(m^3 \cdot g^{-1})$	$(m^3 \cdot g^{-1})$
ZSM-5-bromoadamantane	474	0.353	0.137
ZSM-5-(bromomethyl)cyclohexene	415	0.485	0.118

Table 2. Data of gas molecules physical adsorption.

The Figure 9. showed that ZSM-5-bromoadamantane and ZSM-5-(bromomethyl)cyclohexene have type I adsorption-desorption isotherms, indicating microporous structures. The slope of ZSM-5-bromoadamantane was larger than that of ZSM-5-(bromomethyl)cyclohexene in the relative pressure range of 0.5-0.9, indicating a higher external surface area. The external specific surface areas of ZSM-5-(bromomethyl)cyclohexene and ZSM-5-bromoadamantane were 415 m²·g⁻¹ and 474 $m^2 \cdot g^{-1}$, respectively (Table 2). Usually, the larger the external specific surface area is, the smaller the crystalline particle size. Therefore, ZSM-5-bromoadamantane had a smaller particle size, which was consistent with the results of SEM and TEM characterization. In addition, ZSM-5-(bromomethyl)cyclohexene displayed a larger total pore volume (0.485 m³·g⁻¹) vs. 0.353 m³·g⁻¹) than that of ZSM-5-bromoadamantane, and ZSM-5-bromoadamantane showed a larger micropore volume (0.137 m3·g-1 vs. $0.118 \text{ m}^3 \cdot \text{g}^{-1}$) than ZSM-5-(bromomethyl)cyclohexene.

3.2 Catalytic reactions

The oxidation reactions were performed with the synthesized ZSM-5 catalyst (25 mg), 1-hexene (5 mmol), and H_2O_2 (5 mmol) in methanol (5 ml) in a 20 ml glass reactor in a 60 °C oil bath with stirring for 2 h. After the reaction, the mixture was analyzed by gas chromatography with SE-30 capillary column and FID detector.

3.3 Applications of Plastic Degradation

The synthesized molecular sieves were labeled as HZSM-5-bromoadamantane and HZSM-5-(bromomethyl)cyclohexene by ion exchange. Then 1 g of low-density polyethylene (LDPE) particles and 50 mg of HZSM-5 molecular sieve were added to the specific sized quartz tube reactor, the quartz tube was placed in a specific sized tube furnace, purged with nitrogen for 10 minutes, and then programmed a heating rate of

Graduation Design (Thesis) of the 22nd Undergraduate Course of Qilu University of Technology

5 °C/min. Warmed up to 380 °C, remained constant temperature reaction for degrading for 60 minutes, collected the cooled degradation product after the reaction, dilute the collected product with tridecane, and analyze the product component distribution by gas chromatograph.

	Tempeature (K)	Cracke d(mg)	Degraded(mg)	Sample 1(g)	Sample 2(g)	LDPE(g)	Degraded LDPE(g)	Degrading rate
HZSM-5-bromoadamant ane	653	15	35	40.1611	39.2009	1.0064	0.9602	95.41%
HZSM-5-(bromomethyl) cyclohexene	653	15	35	40.1703	39.1836	1.0065	0.9867	98.03%

The results showed in Table 3.

Sample 1: Total weight before the reaction.

Sample 2: Total weight after the reaction.

The data showed that the synthesized molecular sieves have good efficiency in catalyzing the decomposition of LDPE.

Chapter 4 Conclusions and Outlook

At present, the fossil energy crisis is an important problem facing the world, and the efficient use of fossil energy is an effective way to solve this problem. This puts forward higher requirements for the creation of molecular sieve catalytic materials. The pore size of molecular sieves is small (<2 nm), and the single and narrow pore structure limits the diffusion and transport of reactant/product molecules, and the products cannot diffuse in time, resulting in carbon deposition, resulting in the loss of catalytic activity of molecular sieve materials. Especially when the kinetic size of the reactant molecule is close to or larger than the pore size of the crystal. Due to their larger specific surface area, shorter channel length, and more exposed catalytically active sites, nano- and hierarchically porous molecular sieves can significantly improve the catalytic lifetime and catalytic efficiency of molecular sieves. However, the nano- and hierarchically porous molecular sieves prepared by the current methods are usually polycrystalline, with poor crystallinity and thermal stability, low solid yield, high synthesis cost, etc., which are not conducive to catalytic reactions and industrialization.

Designing different types of quaternary ammonium salt compounds and controlling the reaction conditions can control the crystal morphology of molecular sieves to a certain extent. The synthesis strategy of nano-thin-layer molecular sieves and the design of structure-directing agents also provide new ideas for the development of new materials. In this paper, a new strategy for the synthesis of ZSM-5 molecular sieves with end-capped quaternary ammonium salt structure-directing agents was verified, and high-quality ZSM-5 molecular sieves were prepared. They have the advantages of high yield, high crystallinity, good dispersibility, controlled silicon-to-aluminum ratio, and controllable mesopore size. In this paper, the crystal morphology, size, and structure of the molecular sieve were characterized, and the catalytic performance was verified by the catalytic reaction.

References

[1] Baerlocher C, McCusker L B, Olson D H, Atlas of Zeolite Framework Types. Elsevier, 2007.

[2] Díaz I, Kokkoli E, Terasaki O, Tsapatsis M, Surface Structure of Zeolite (MFI) Crystals. Chemistry of Materials 2004

[3] Min Y.Y, Shang Y.S, Song Y, Li G.D, Gong Y.J, The Synthesis of Nanosheets Zeolite and Its Catalytic Application. Progress in Chemistry 2015

[4] Vojoudi H, Badiei A, Bahar S, Ziarani GM, Faridbod F, Ganjali MR. A new nano-sorbent for fast and efficient removal of heavy metals from aqueous solutions based on modification of magnetic mesoporous silica nanospheres. Journal of magnetism and magnetic materials. 2017

[5] Zhang Y, Su Z, Li B, Zhang L, Fan D, Ma H. Recyclable magnetic mesoporous nanocomposite with improved sensing performance toward nitrite. ACS Applied Materials & Interfaces. 2016

[6] Li X, Zhu Y, Ma Y, Ren H, Wu D, Yang Y, Shao Y, Wei X, Zhao J. Nitrite optical sensing from core-shell structured nano sensors functionalized with rhodamine molecules. Journal of Luminescence. 2018

[7] Li J, Wu Y, Yang C, Zhu R, Zhao K. For the optical detection of anthrax biomarker using a luminescent rare earth-organic framework modified by rhodamine molecules: Synthesis, characterization and two sensing channels. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy. 2018

[8] Wang Y, Zhu L, An L. Electricity generation and storage in microbial fuel cells with porous polypyrrole-base composite modified carbon brush anodes. Renewable Energy. 2020

[9] Darwish M, Mohammadi A. Functionalized nanomaterial for environmental techniques. Nanotechnology in Environmental Science. 2018

[10] Ghasemi M, Daud WR, Hassan SH, Oh SE, Ismail M, Rahimnejad M, Jahim JM. Nano-structured carbon as electrode material in microbial fuel cells: A comprehensive review. Journal of Alloys and Compounds. 2013

[11] Li X M. Porous Nanomaterials and Application. Chemical Industry Press, 2020

[12] Huang F, Yan M, Wang L, etc. Application of Nanomaterials in Medical Field [J]. Guangzhou Chemical Industry, 2020

[13] Gunputh U F, Le H R, Lawton K. et al., antibacterial properties of silver nanoparticles grown in situ and anchored to titanium dioxide nanotubes on titanium implant against Staphylococcus aureus [J]. Nanotoxicology, 2020

Graduation Design (Thesis) of the 22nd Undergraduate Course of Qilu University of Technology

[14] Hu H, Deng C, Sun M, et al. Facile template-free synthesis of hierarchically porous NiO hollow architectures with high-efficiency adsorptive removal of Congo red[J]. Journal of Porous Materials, 2019

[15] Li Y, Wang H, Xie L, et al. MoS2 nanoparticles grown on graphene: an advanced catalyst for the hydrogen evolution reaction[J]. Journal of the American Chemical Society, 2011

[16] Tsai M L, Su S H, Chang J. K. et al. Monolayer MoS2 Heterojunction Solar Cells [J]. ACS Nano, 2014

[17] He X, Wang R, Peng Q, Jiao W, Zhao X. Research progress of nano-carbon composites for aerospace [J]. Astronautics, 2020.

[18] Peng Q Y, Li Y B, He X D, et al. Graphene nanoribbon aerogels unzipped from carbon nanotube sponges[J]. Advanced Materials, 2014

[19] Xie Q. Introduction to Advances in X-ray Diffraction: Physics, 2012

[20] Brunauer, Stephen; Emmett, P. H.; Teller, Edward. "Adsorption of Gases in Multimolecular Layers". Journal of the American Chemical Society, 1938

[21] Hanaor, D. A. H.; Ghadiri, M.; Chrzanowski, W.; Gan, Y. "Scalable Surface Area Characterization by Electrokinetic Analysis of Complex Anion Adsorption",2014

Acknowledgements

Enrolling in this double degree program has been a truly life-changing experience for me and it would not have been possible without the encouragement, support, and guidance that I received from all of you.

First and foremost, I would like to thank my supervisor Prof. Wang Jingui, for accepting me to work in his group. He is a respected leader who really advises and promotes students. I am sincerely grateful to him for his continuous support from our first Inorganic Chem. lecture, his kindness, scientific guidance, and constructive criticism, and thankful for less serious chats and jokes.

Besides, I would like to express my sincere gratitude to all my teachers during my four years of undergraduate life both in China and Finland. In particular, I would like to thank Prof. Li Tianduo, and Ms. Li Yan for strongly supporting and encouraging me to join the international class and study abroad.

I would like to express my special appreciation and thanks to my tutor Ms. Wang Hongjuan, for being our headteacher, for teaching me to change mindsets and to solve problems, and for her words just like a mother telling her kid.

Kiitos paljon! To Ms. Mirja Onduso, you have always been there selflessly helping me in my hour of darkness and directing my passage, I could not be that determined and independent without your words of recognition.

I would like to thank the senior students in our lab. Thanks to Dashixiong Fu Kairui for carrying me with the lab work, and thanks to Xu Fulin and Zhang Bin who have always been patient to answer my questions even though some of them were nonsense.

I would say thanks to Mr.Jerrell Tom Asbill, when I was in a down mood, he always accompanying with me and give me advice of life.

I would thank all my friends, you guys make me who I am by far.

Last but not least, I want especially to thank my beloved family for believing in me and for their never-ending support and love!

While writing this thesis, I am facing the choice of deciding where to pursue my master's, it was a tough and exciting decision. When standing at roads diverged in life, I firmly believe whatever it is, that has made all the difference.