

Research and Application Progress of Mesoporous Materials Synthesized by Rosin-based Surfactant Template

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Abstract: Rosin is a kind of important natural chemical materials which can be regenerated naturally, and it is widely used. The synthesis of surfactants from rosin is one of the main ways of deep processing. Rosin is easy to modify because it contains carbon-carbon double bonds and carboxyl active groups. A series of rosin-based surfactants can be synthesized through the modification of rosin. Rosin-based surfactants are widely used in the synthesis of nanomaterials and mesoporous materials due to their special three-membered phenanthrene frame structure. Therefore, in this article the application of rosin-based template synthesis of mesoporous materials was summarized in detail, which mainly included from the aspects of rosin composition and structure, modified synthetic surfactants and mesoporous materials used for synthesis, and existing problems. Combined with the application status of rosin series surfactants, the future research direction and development trend of new rosin-based surfactants are prospected.

1. Introduction

According to the definition of International Union of Pure and Applied Chemistry (IUPAC), ordered porous materials can be divided into three categories according to their pore size [1]: less than 2 nm is micropore; 2 ~ 50 nm is mesopore; more than 50 nm is macropore. Because of its unique pore structure, excellent physical and chemical properties, and potential applications, mesoporous materials have aroused great interest, and have always become a research hotspot in the material industry, and its application fields have been continuously developed and expanded [2-3].

As we all know, the template method is a typical method of synthesizing mesoporous materials. Among them, the soft template method is one of the most commonly used methods for synthesizing mesoporous materials, because amphiphilic surfactants are often self-assembled into mesoporous materials under acidic or alkaline conditions. Due to the presence of surfactants, it is easy to adjust the morphology of the materials, pore size and mesopore structure, particle size.

In the synthesis of mesoporous materials, silicon oxide materials with different mesoporous structure phases can be synthesized using different types and structures of directing agent templates. Among the most commonly used templates are amphiphilic surfactant molecules (such as alkyl

quaternary ammonium surfactants), block copolymers, microemulsion templates, bacterial templates, etc. [4-8]. The surfactant templates currently used in different mesoporous phases are mainly cationic surfactants, anionic surfactants and nonionic surfactants, and mixed surfactants. The type and molecular structure of surfactants have a great influence on the formation of various mesoporous materials. In order to develop new surfactants with special properties of new structures, researchers are constantly seeking and exploring new structure-directing agents on the chance of preparing porous materials with diverse structures and properties. Among them, the rosin-based template has become a hot spot for continuous exploration and research, which is based on the special structure of rosin and the reason for easy modification. Therefore, in this article the composition, structure, modification of rosin and the research situation of mesoporous materials synthesized by rosin-based template were generalized.

2. Composition and structure of rosin

Rosin is a renewable resource and it is widely used. It is a mixture of various resin acids, a small amount of fatty acids, and neutral substances. Its main component is resin acid, which accounts for about 90% of its total. Resin acid is the general name of a class of isomers with molecular formula $C_{19}H_{29}COOH$ (as shown in Table 1). The main types, structure and reactivity of resin acids were showed in Table 1. They are abietic acid, levopimaric acid, neoabietic acid, longleaf abietic acid and dehydroabietic acid respectively, which contain a three-membered ring phenanthrene framework, two double bonds and a carboxyl group. Due to the special structure of rosin, various atoms or groups can be introduced through the two reactive centers of double bond and carboxylic acid to obtain different structures and types of rosin, which can be used in various industries such as chemical industry, medicine, ink, perfume.

Table 1 Types, structure and reactivity of resin acids

Types	Molecular Formula	Structural Features	Reactivity
Abietic acid	$C_{19}H_{20}COOH$	Three-membered phenanthrene frame structure, two unsaturated carbon-carbon double bonds (-C = C-, in the ring, located at 7, 8; 13, 14 position of C atom) and one carboxyl group (-COOH, located at 4 position of C atom)	Isomerization, addition, polymerization, hydrodehydrogenation, disproportionation and oxidation reactions.
Levopimaric acid	$C_{19}H_{20}COOH$	Three-membered ring phenanthrene structure, two unsaturated carbon-carbon double bonds (-C = C-, in the ring, located at the 8,14; 12,13 position of the C atom) and a carboxyl group (-COOH, located at the 4 position of the C atom)	Isomerization, addition, polymerization, hydrodehydrogenation, disproportionation and oxidation reactions.
Neoabietic acid	$C_{19}H_{20}COOH$	Three-membered ring phenanthrene structure, two unsaturated double bonds (-C = C-, one in the ring, located at 8,14 C atoms; one out the ring, located at 13,15 positions of C atoms) and one carboxyl group (-COOH, At C atom 4 position)	Isomerization, addition, polymerization, hydrodehydrogenation, disproportionation and oxidation reactions.
Longleaf abietic acid	$C_{19}H_{20}COOH$	Three-membered ring phenanthrene structure, two unsaturated double bonds (-C = C-, in the ring, located at 8, 9; 13, 14 position of C atom) and one carboxyl group (-COOH, located at 4 position of C atom)	Isomerization, addition, polymerization, hydrodehydrogenation, disproportionation and oxidation reactions.
Dehydroabietic acid	$C_{19}H_{20}COOH$	Three-membered phenanthrene ring structure, benzene ring structure and carboxyl group (-COOH, located at the 4 position of C atom)	The nature is more stable (compared to the above)

3. Rosin modified synthetic surfactant

Rosin has active groups -C = C- double bond (conjugated and non-conjugated) and -COOH carboxyl functional groups, a series of rosin derivatives can be synthesized by introducing various atoms or groups after modification [9-11]. Rosin derivative surfactants, as a class of functional chemicals, which play an important role in various fields.

With the development of circular economy and ecological value ideas are put forward, the development and production of renewable and easily degradable biomass resources has become a research hotspot. Rosin is a kind of natural and renewable resource which can be utilized fully, and the research and development of rosin should be increased. Use the rosin as the basic raw material, a new type of rosin-based surfactant can be synthesized, and the variety of surfactant can be enriched, it is very important to reduce the dependence on oil and natural oil [12-13]. At present, research on the synthesis of surfactants using rosin as a raw material has achieved good results. Various biodegradable properties have been synthesized, which have a wide range of applications, high value-added products, and good surface properties. Such as common surfactants there are cationic surfactants, anionic surfactants, nonionic surfactants and gemini surfactants. The following mainly introduces several common surfactants.

3.1 Rosin based quaternary ammonium cationic surfactant

Table 2 Types and characteristics of rosin-based quaternary ammonium cationic surfactants

Name	Raw Material	Synthesis Method	CMC (mo l/L)	Surface Tension (mN/m)	Emulsifying Properties (min)	References
Dichlorinated-N-N'-bis(3-rosinyloxy-2-hydroxypropyl)-tetramethylethylenediamine	Rosin acid, Epichlorohydrin, Tetramethylethylenediamine	Two-step synthesis	1.42×10^{-4}	36.69	16	[14]
N-Dehydroabietyl-N,N-dimethyl-N-hydroxyethyl ammonium chloride	Dehydroabietylamine, Chloroethanol	One-step synthesis	3.45×10^{-3}	33.2	10.0	[15]
N,N-dimethyl-N-benzyl-N-dehydroabietyl ammonium chloride	Dehydroabietylamine, benzyl Chloride	Two-step synthesis	5.06×10^{-3}	36.6	13.0	[16]
Di-(N-dehydroabietyl-N,N-dimethyl)-N,N'-(1,3-propylene) diammonium bromide	Dehydroabietylamine, 1,3-Dibromopropane	Two-step synthesis	2.1×10^{-5}	Nr	22.0	[17]
Rosin based quaternary ammonium salt Gemini surfactant	Dehydroabietylamine, Dibromoalkane	Two-step synthesis	$(2.5 \sim 5.5) \times 10^{-5}$	23.7~ 30.3	50.0	[18]
Rosin based quaternary ammonium salt Gemini surfactant	Rosin acid, Epichlorohydrin, Tetramethylpropanediamine	Two-step synthesis	4×10^{-4}	37.25	20.0	[19]
N, N, N', N'-Tetramethyl-N-dehydroabietyl-N'-dodecyl-dibromide-1,5-penta mmonium	Dehydroabietic acid, Dodecyl dimethyl tertiary amine, Dibromoalkane	Multi-step synthesis	2.54×10^{-5}	28.9	53.0	[20]
Rosin-based choline quaternary ammonium salt surfactant	Dehydroabietic acid, choline	One-step synthesis	6.9×10^{-3}	37.9	8.1	[21]
N, N'-bis(3-rosinyloxy-2-hydroxypropyl)-tetrahydroxyethylbutanediamine dichloride	Rosin acid, Epichlorohydrin, Diethanolamine, 1,4-Dibromobutane	Multi-step synthesis	3.8×10^{-5}	36.8	27.0	[22]
Rosin-based double quaternary ammonium salt type cationic surfactant	Rosin acid, Acrylic acid, Epichlorohydrin, pyridine	Two-step synthesis	5.3×10^{-4}	Nr	42.0	[23]
3-rosin acyloxy-2-4-	Rosin acid,	Two-step	3.7×10^{-5}	35.9	29.0	[24]

hydroxypropyl-N, N, N-trimethylammonium chloride	Epichlorohydrin, Trimethyl amine	synthesis				
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Note: CMC — critical micelle concentration; Nr — not reported

By sorting out the literature, the relevant data obtained is shown in Table 2. The analysis data found that a large amount of rosin-based quaternary ammonium surfactants have been synthesized, and its performance analysis and application research have been carried out. Through the introduction of various hydrophilic groups, a series of excellent and unique surfactants are prepared. Rosin series surfactants combine the basic properties of rosin with the advantages of new ionic groups and composite functional groups, which make their structural properties more novel and biodegradable. It can be seen from Table 2 that many different types of rosin-based quaternary ammonium salts are synthesized, but the synthetic routes and methods are more complicated. However, the researchers have explored the best process conditions, measured and analyzed the product performance parameters such as critical micelle concentration (CMC), surface tension and emulsifying property indicated that the product has good efficiency and ability to reduce surface tension, which is equivalent to the emulsifying ability of the traditional surfactant cetyltrimethylammonium bromide (CTAB) [22]. The performance parameters of various rosin-based quaternary ammonium salts are different, which is related to the introduced groups. It can be seen from the data analysis results in Table 2 that the use of rosin as a raw material can not only prepare a common surfactant with a single hydrophilic group and a single hydrophobic group, but also prepare a double hydrophilic group and a double hydrophobic group gemini with high surface activity and low CMC type surfactant. The quaternary ammonium salt surfactant prepared with rosin base has good water solubility, and shows excellent performance in daily chemical industry, dyeing and spinning industries, and is widely used in chemical, pharmaceutical, and material synthesis fields [25].

3.2 Rosin-based amphoteric surfactant

There are few types of amphoteric surfactants synthesized from rosin. The amphoteric surfactants have the characteristics of good detergency, strong emulsifying ability, stability to acids and alkalis and various metal ions, and easy biodegradation etc. Zhao Yinfeng et al. [26] used dehydroabiatic acid as the raw material and used a two-step synthesis method to prepare 3-rosin acyloxy-2-hydroxypropyl chloride and tertiary amine intermediates before synthesizing N-(3-dehydroabiatic acid Oxygen-2-hydroxy) propyl-N, N-dimethyl (2-hydroxy) phosphate betaine surfactant. After characterization analysis, the results show that the critical micelle concentration (CMC) is $1.34 \times 10^{-3} \text{ mol / L}$, and the surface tension is 38.69 mN / m . At the same time, Zhao Yinfeng et al. [27] used the same synthesis method to synthesize quaternary ammonium salt intermediates by reacting dehydroabiatic acid with epichlorohydrin and trimethylamine, and then synthesizing dehydroabiatic amphoteric surfactant with concentrated sulfuric acid. The CMC of the prepared dehydroabiatic amphoteric surfactant was $1.39 \times 10^{-3} \text{ mol/L}$, and the surface tension was reduced to 21.308 mN/m , indicating that the dehydroabiatic amphoteric surfactant had a certain surface activity.

3.3 Non-quaternary ammonium salt type rosin-based surfactant

In the synthesis of rosin-based surfactants, the introduction of N, O and S heteroatom groups can enhance the hydrophilic properties of molecules and give them excellent surface properties [28]. The introduced heteroatoms N, O and S have a lone pair electron special function structure, which make their performance better than other surface activities. Non-quaternary ammonium salt

surfactants synthesized with rosin as raw materials are low in cost and environmentally friendly, which is the focus of future research on functional surfactants.

4. Mesoporous material synthesized by rosin-based template

Rosin series surfactants are very versatile and can be used as emulsifiers, detergents, bactericides, wetting agents and viscosity reducers. At present, rosin-based has played an important role in the synthesis of nano-functional materials and mesoporous materials [29]. According to reports in the literature, mesoporous materials modified by rosin have achieved considerable results. Therefore, the following mainly introduces various mesoporous and porous materials synthesized using rosin-based surfactants as a template.

4.1 Synthetic mesoporous silica

Table 3 Performance parameters of mesoporous silica synthesized with different rosin based templates

Template type	Raw Material	Synthesis method	Particle Size (nm)	BET Specific Surface area (m^2/g)	Pore Volume (cm^3/g)	Pore Diameter (nm)	References
Rosin Derivative Gemini Surfactant	Ethyl orthosilicate	Sol-gel method	30	116.83	0.45	29.8	[30]
Rosin-based double quaternary ammonium salt and CTAB as a blending template	Ethyl orthosilicate	Sol-gel method	Nr	685.29	1.22	3.5	[31]
Ethylenediamine-dirosinylglycine gemini surfactant	Ethyl orthosilicate	Sol-gel method	30	116.83	0.45	15.31	[32]
Ethylenediamine-dirosinylglycine gemini surfactant	Ethyl orthosilicate	Microemuls-ion	30-50	928.10	1.04	4.49	[32]
Dehydroabietyltrimethylammonium bromide	Ethyl orthosilicate	Hydrotherm-al synthesis	Nr	1097.59	0.63	1.91	[33]
Dehydroabietyltrimethylammonium bromide	Sodium silicate	Hydrotherm-al synthesis	Nr	1299.15	0.59	2.03	[33]

Note: Nr — not reported

According to the references [30-33], the performance parameters of mesoporous silica synthesized by different rosin-based templates were obtained (as shown in Table 3). It can be seen from Table 3 that using different rosin-based template agents and ethyl orthosilicate as the silicon source, high specific surface areas ($1299.15\text{m}^2/\text{g}$) and large pore volume ($1.22\text{cm}^3/\text{g}$) can be prepared by different synthesis methods), Amorphous mesoporous silica with uniform pore size and adjustable pore size (1.91~29.8nm), which reflects the excellent template performance of rosin-based surfactants, and mesoporous silica prepared with traditional surfactant CTAB is quite [2-3]. From the perspective of the synthesis mechanism of mesoporous materials, in the process of synergistic self-assembly of surfactants and inorganic species to form mesoporous structures, the properties of surfactants (including charge density, size, shape, charge type, etc.) plays a decisive role for the structure of mesoporous materials. Different types of surfactants will form mesoporous materials with different structures in the same reaction system. In the process of preparing mesoporous materials with rosin-based templates, rosin-based quaternary ammonium salt surfactants have the same lipophilic and hydrophilic groups as the traditional surfactant CTAB, which easily aggregate to form micelles in the synthesis reaction system. Organic-inorganic cooperative self-assembly between inorganic silicon oligomers is beneficial to the formation of mesoporous SiO_2 materials. Therefore, through the interfacial interaction between the rosin-based quaternary ammonium salt and ethyl silicate, a silica material with a porous structure is

self-assembled. It can be seen from the data in Table 3 that some of the prepared mesoporous silica particles are in the form of small nano-sized particles with a particle size of about 30 nm. This may be due to the fact that the rosin-based quaternary ammonium salt surfactant structure contains a ring structure. The three-ring phenanthrene skeleton hydrophobic chain has a large steric hindrance effect, thereby avoiding agglomeration between silica particles.

4.2 Synthetic mesoporous titanium dioxide

Han Shiyan [32] used tetrabutyl titanate as raw material, and used ethylenediamine-didehydroabietyl glycine gemini surfactant as a template to prepare nano-sized titanium dioxide by hydrothermal synthesis, with a particle size of about 5.5 nm. Degradation of rhodamine (RhB) by photocatalysis, its degradation rate can reach 99.7%, almost complete degradation. The dispersion between the particles is good and there is no agglomeration, indicating that in the preparation of titanium dioxide, the ethylenediamine-didehydroabietic acid glycine gemini surfactant has a good dispersion effect between the nanoparticles, preventing the agglomeration between the nanoparticles, And effectively control the size of the particles.

Wang Peng [33] used dehydroabietyl trimethylammonium bromide as the structure guide agents and peroxytitanate as the titanium source to synthesize highly ordered layered mesoporous titanium dioxide in the medium of tetramethylammonium hydroxide. The pore size of the obtained material is about 2 nm, and the thickness of the pore wall is about 1 nm. Also, using tetrabutyl titanate as the titanium source, the semi-crystalline anatase phase uniform mesoporous titanium dioxide was synthesized by the volatilization-induced self-assembly method. The materials prepared showed worm-like mesoporous channels with long-range disorder but uniform pore diameter. The pore size is about 2 nm, and the wall thickness is about 1 nm. The above results showed that the new rosin-based cationic surfactant dehydroabietyl trimethylammonium bromide could synthesize the mesoporous titanium dioxide. Its unique rigid tricyclic phenanthrene structure hydrophobic group is very different from the traditional long-chain hydrophobic group. The mesoporous titanium dioxide material has a unique structure.

Zhao Yinfeng et al. [34] used a dehydroabietyl amphosurfine phosphate amphoteric surfactant as a template agent and $TiCl_4$ as a titanium source to prepare porous TiO_2 using acid-catalyzed hydrolysis. It has a typical mesoporous structure with a pore size of 11.46 nm, with type IV adsorption isotherm, the degradation rate of p-phenol is 73.06%, and the porous structure improves the adsorption performance of TiO_2 . In addition, porous TiO_2 was prepared by acid-catalyzed hydrolysis using dehydroabietyl trimethyl quaternary ammonium salt cationic surfactant as the template agent. The obtained porous TiO_2 has a typical mesoporous structure and a typical type IV adsorption isotherm. The diameter of the pore is 12.38nm. After calcination, the sample is completely in the structure of Ruiqin ore phase and its grain size is 12.6nm. The photocatalytic activity test of the prepared sample shows that the degradation rate of phenol is 74.21%.

4.3 Synthetic mesoporous aluminum oxide

Table 4 Performance parameters of mesoporous aluminum oxide synthesized with different surfactants

Template type	Raw Material	Synthesis method	Surfactant amount (g)	BET Specific Surface area (m^2/g)	Pore Volume (cm^3/g)	Pore Diameter (nm)	References
Rosin	Aluminum	Hydrothermal-precipitation	0.8	194.07	0.27	4.18	[35-36]

trimethylammonium chloride	nitrate	method					
Rosin trimethylammonium chloride	Aluminum nitrate	Hydrothermal-precipitation method	1.6	213.33	0.32	5.03	[35-36]
Rosin trimethylammonium chloride	Aluminum nitrate	Hydrothermal-precipitation method	2.0	209.56	0.32	5.02	[35-36]
Rosin trimethylammonium chloride	Aluminum nitrate	Hydrothermal-precipitation method	2.4	209.31	0.32	5.18	[35-36]

Wang Peng et al. [35-36] used industrial rosin-based trimethylammonium chloride as the structure guiding agent to synthesize uniform mesoporous γ -Al₂O₃ by ammonium carbonate precipitation method, and prepared rosin-based quaternary ammonium salt as the structure guiding agent to synthesize the uniform mesoporous alumina. Experiments in the literatures investigated the effect of surfactants addition on the pore structure of alumina. According to the literatures, the performance parameters of mesoporous aluminum oxide synthesized with different surfactant addition amounts are cited (as shown in Table 4). The obtained samples were mesoporous γ -Al₂O₃, the specific surface areas was 194~213 m²/g, and the average pore diameter was 4.18~5.18 nm. The pore volume is 0.27~0.32cm³/g. It can be seen from Table 4 that the amount of rosin-based quaternary ammonium salt has a great influence on the structural properties of alumina. The appropriate amount of rosin-based quaternary ammonium salt is beneficial to alumina to obtain a larger pore size and a narrower pore size distribution. This is consistent with the effect of the amount of traditional surfactant on the mesoporous phase structure. At the same time, the specific surface area, pore volume and pore size of uniform mesoporous γ -Al₂O₃ were improved by the ammonia precipitation method.

Table 5 Performance parameters of mesoporous aluminum oxide synthesized under different reaction temperatures

Template type	Raw Material	Synthesis method	Reaction Temperature (K)	BET Specific Surface area (m ² /g)	Pore Volume (cm ³ /g)	Pore Diameter (nm)	References
Rosin trimethylammonium chloride	Aluminum nitrate	Hydrothermal-precipitation method	363	179.75	0.47	8.84	[35-36]
Rosin trimethylammonium chloride	Aluminum nitrate	Hydrothermal-precipitation method	373	241.18	0.36	7.21	[35-36]
Rosin trimethylammonium chloride	Aluminum nitrate	Hydrothermal-precipitation method	383	231.50	0.38	8.47	[35-36]
Rosin trimethylammonium chloride	Aluminum nitrate	Hydrothermal-precipitation method	393	216.16	0.45	8.10	[35-36]

In addition, the literatures also investigated the effect of hydrothermal reaction temperature on the pore structure of alumina. It was found that the temperature of the hydrothermal reaction has a great influence on the microstructure of the sample. The detailed data is shown in Table 5. When the

hydrothermal temperature is 373 K, the specific surface area of the sample is relatively large ($241.18\text{m}^2/\text{g}$), but the pore size is relatively small (7.21nm). Increase or decrease of the hydrothermal reaction temperature of the sample will cause the specific surface areas of the samples to decrease, but the pore size of the sample will increase. The precursor fiber obtained at a hydrothermal temperature of 373 K has a length of about 5 μm and a width of about 200 nm. After calcination, the sample morphology is preserved and the porosity is increased. The above results indicate that the rosin-based quaternary ammonium salt structure directing agent exhibits excellent template behavior in the synthesis of non-silicon-based mesoporous materials.

4.4 Other mesoporous materials

According to the literature reports, Wang Peng [36] used dehydroabietyltrimethylammonium bromide (DTAB) as the structure guide agent, and zirconium sulfate ($\text{Zr}(\text{SO}_4)_2$) as the source of zirconium, synthesized by a strong alkaline hydrothermal method pure tetragonal phase nanocrystalline mesoporous zirconium dioxide is produced. The synthesized tetragonal phase nanocrystalline mesoporous zirconium dioxide has a high specific surface ($107.34\sim 242.02\text{m}^2/\text{g}$) and pore volume ($0.25\sim 0.53\text{cm}^3/\text{g}$) and a large pore diameter (6.06~12.96 nm). The above results showed that while maintaining such a large pore size, mesoporous zirconia material also has a high specific surface area and pore volume, which was rare, indicating that the synthesis of zirconia materials guided by DTAB have a great advantages, reflecting the structural characteristics of the template agent. At the same time, the literatures examined the effect of different DTAB additions on the pore structure of zirconium dioxide. The addition of DTAB (0.025, 0.05, 0.075, 0.1), the pore structure parameters of the obtained samples were, specific surface area (121.92, 152.92, 145.11, $122.79\text{m}^2/\text{g}$) and pore volume (0.25, 0.48, 0.39, $0.32\text{cm}^3/\text{g}$) and larger pore size (6.06, 9.89, 8.10, 7.66nm). Increasing or decreasing the amount of DTAB will cause the sample pore size and pore structure performance to decline, indicating that only a suitable amount of surfactant added can help the sample to form a larger pore size, which is consistent with the previous report.

5. Conclusion

After years of development, the synthesis and application of rosin-based quaternary ammonium surfactants have been extensively studied. A variety of different types of rosin-based quaternary ammonium salts are synthesized and show excellent performance in daily chemical, dyeing and spinning industries. However, there are many problems to be solved in the aspects of rosin-based quaternary ammonium salt surfactants in the optimization of synthesis process, mesopore formation mechanism exploration, thermodynamic research, molecular structure innovation, and new application fields.

Although good progress has been made in synthesizing mesoporous materials using rosin-based templates, there are still many problems that need to be solved urgently. First of all, the synthesis routes of some rosin-based templates are complex, the separation and purification are more difficult, and the production cost is higher; secondly, at present, rosin-based is used to synthesize mesoporous materials of few types (especially non-silicon-based mesoporous materials), which needs to be developed and synthesized. Other types of mesoporous materials, and in the process of synthesizing mesoporous materials, there are few studies on the formation mechanism of mesoporous materials synthesized with rosin-based templates; in addition, currently studies on the micellization behavior of rosin-based surfactants and on the thermodynamic and kinetic mechanisms of forming microstructures are few reports. Again, it is difficult to synthesize long-range ordered mesoporous materials with rosin-based templating agents. It is necessary to further optimize the structural design and performance of rosin-based stencils, or develop new rosin-based templating agents in order to

synthesize highly ordered mesoporous material. Finally, the application fields of rosin templating agents are mostly concentrated in traditional daily-use chemicals, inks, papermaking, textiles, etc., but there are few practical applications in emerging technical fields such as ecological environmental protection, biopharmaceuticals, and functional materials. Therefore, in the future research, researchers are expected to continue to carry out the synthesis of new structure rosin-based surfactants on the one hand, and on the other hand, they should expand the application field for the characteristics of the base structure.

Rosin is a huge natural renewable resource, so it is of great significance to carry out the synthesis of rosin-based templating agent using rosin as the basic raw material for the synthesis of mesoporous materials, nanomaterials and functional materials. In response to the above-mentioned problems with rosin-based templates, researchers should increase their efforts to optimize their structural design and performance, and use modifiers that are simple in process and easy to synthesize to optimize rosin. It is important to improve the synthesis process of existing products, seek the best synthesis conditions, reduce production costs, and reduce environmental pollution in the production process. In particular, it is important to synthesize a new type of rosin green environmentally friendly template agent with unique properties. While carrying out the synthesis work of the new structure rosin-based template agent, the application field of rosin-based structural characteristics should be expanded. With the continuous research and exploration of rosin-based functional monomers, a series of new surfactants synthesized from rosin-based derivatives will be developed, which provides new resources for the development of new materials in the field of natural materials such as rosin. The opportunity is particularly prominent in the application of surfactant functional materials. This shows that its application in the field of functional materials will have huge development prospects. In short, the rosin-based template has a potentially broad application prospect.

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References

- [1] Xu Ruren, Pang Wenqin, etc. *Molecular sieve and porous material chemistry [M]*, Beijing: Science Press, 2004.
- [2] C.T. Kresge, M.E. Leonowicz, W.J. Roth, et al. *Ordered Mesoporous Molecular Sieves Synthesized by a Liquid-Crystal Template Mechanism [J]*. *Nature*, 1992, 359: 710-712.
- [3] J.S. Beck, J. C. Vartuli, W.J. Roth et al. *A New Family of Mesoporous Molecular Sieves Prepared with Liquid Crystal Templates [J]*. *J. Am. Chem. Soc.*, 1992, 114: 10834-10843.
- [4] Zhao Guoxi, Zhu Buyao. *Principle of surfactant action [M]*, Beijing: China Light Industry Press, 2004.
- [5] J.N. Israelachvili, D.J. Mitchell, B.W. Ninham. *Theory of Self-assembly of Hydrocarbon Amphiphiles into Micelles and Bilayer [J]*. *J. Chem. Soc., Faraday Trans.*, 1976, 72: 1525-1568.
- [6] D.Y. Zhao, J.L. Feng, Q.S. Huo, et al. *Triblock Copolymer Syntheses of Mesoporous Silica with Periodic 50 to 300 Angstrom Pores [J]*. *Science*, 1998, 279: 548-552.
- [7] F. Martinez, Y.J. Han, G. Stucky, et al. *Synthesis and Characterisation of Iron-Containing SBA-15 Mesoporous Silica [J]*. *Studies in Surface Science and Catalysis*, 2002, 142: 1109-1116.
- [8] Cai Xiaohui, Zhu Guangshan, Gao Bo et al. *Preparation and antibacterial properties of Ag / SBA-15 composite materials [J]*. *Chemical Journal of Chinese Universities*, 2006, (27): 2042-2044.
- [9] Li Renhuan, Chen Yuanxia, Huang Kerun. *Research and application overview of rosin carboxyl modification [J]*. *Chemical Technology and Development*, 40 (3): 2011, 17-21
- [10] Sun Dawei, Xu Yongxia, Han Chunrui. *Research and application progress of rosin modified polymer materials [J]*. *Progress in Chemical Engineering*, 32 (3): 2013 599-602

- [11] Wei Xiaohui, Cao De. *Research Progress of Rosin Modified Preparation of Surfactant and Its Application* [J]. *Guangzhou Chemistry*, 29 (1): 2004, 42-49
- [12] Guo Naini, Yang Jianzhou, Li Yu. *Research progress in synthesis of rosin surfactants* [J] *Leather and Chemical Industry*, 25 (6): 2008, 11-14.
- [13] Song Fei, Wang Peng, Wang Zongde, et al. *New progress in the study of rosin-based surfactants* [J]. *Guangzhou Chemical Industry* 43 (10): 2015, 3-7
- [14] Han Shiyan, Song Zhanqian, Jin Zhongling et al. *Synthesis and analysis of rosin-based quaternary ammonium gemini surfactants* [J]. *Forestry Science and Technology*, 34 (4): 2 61-64
- [15] Wang Yan, Song Zhanqian, Liang Menglan. *Synthesis and properties of N-dehydroabietyl-N, N-dimethyl quaternary cationic surfactants* [J]. *Daily Chemical Industry*, 4, 15-17, 1997.
- [16] Liang Menglan, Ye Jianfeng. *Synthesis and performance determination of cationic surfactants of quaternary ammonium salts of rosin derivatives* [J]. *Chemical World*, 3,138-141, 2000.
- [17] Jiang Fubin, Zeng Huahui, Yang Zhengye, et al. *Synthesis and properties of rosin-based quaternary ammonium salt cationic surfactants* [J]. *Fine Chemicals*, 24 (11): 1074-1079, 2007.
- [18] Jia Weihong, Rao Xiaoping, Song Zhanqian, et al. *Synthesis and properties of rosin-based quaternary ammonium salt Gemini surfactants* [J]. *Modern Engineering*, 28 Suppl (2): 390-394, 2008.
- [19] Wang Haifeng, Jiang Zanguo, Ma Yuling et al. *Synthesis and analysis of new rosin-based Gemini surfactants* [J]. *Modern Engineering*, 32 (5): 2012, 79-81.
- [20] Wang Juan, Wang Dan, Shang Shibin et al. *Synthesis and properties of rosin-based quaternary ammonium salt gemini surfactants* [J]. *Forest Products Chemistry and Industry*, 34 (6): 2014, 111-116
- [21] Zheng Jianqiang, Liu Li, Rao Xiaoping, et al. *Synthesis and bacteriostatic activity of rosin-based choline quaternary ammonium surfactants* [J]. *Forest Products Chemistry and Industry*, 35 (5): 98-104, 2015.
- [22] Wang Kaiming, Zhang Yongchang, Li Miao, et al. *Synthesis and properties of a new type of rosin-based quaternary ammonium salt Gemini surfactant* [J]. *Printing and Dyeing Auxiliaries*, 28 (11): 9-12, 2011.
- [23] Wei Xiaohui, Liao Shizhen, Cao Derong, et al. *Synthesis and properties of rosin-based quaternary ammonium salt cationic surfactants* [J]. *Fine Chemicals*, 20 (9): 557-560, 2003.
- [24] Guo Naini, Yang Lianli. *Synthesis and properties of a new quaternary ammonium salt rosin surfactant* [J]. *Leather and Chemical Industry*, 33 (3): 17-20, 2016.
- [25] Xu Lifeng, He Fenghua, Wang Peng et al. *Research progress in the synthesis of rosin-based quaternary ammonium surfactants* [J]. *Guangdong Chemical Industry*, 41 (15): 111-113.
- [26] Zhao Yinfeng, Fang Guizhen, Ma Yingmei, Ma Yanli, Jin Zhongling, *Synthesis and Characterization of Dehydroabietyl Betaine Amphoteric Surfactant* [J]. *Modern Engineering*, 30 (7): M2010, 44-47
- [27] Zhao Yinfeng, Fang Guizhen, Ai Qing et al. *Synthesis of amphoteric surfactants based on dehydrogenated rosin* [J]. *Journal of Northeast Forestry University*, 38 (2): 201088-90.
- [28] Xu Yongxia, Li Juan, Li Baotong. *Research progress of non-quaternary ammonium salt-based rosin-based surfactants* [J]. *Material Report A: Review*, 30 (1): 2016, 61-66
- [29] Zhang Guoyun. *Synthesis and application of rosin series surfactants* [J]. *Daily Chemical Industry*, 34 (4): 2004, 105-107
- [30] Ma Yuling, Shang Xuting, Cui Shufen, et al. *Characterization of porous silica prepared with rosin modification as template* [J]. *Forest Products Chemistry and Industry*, 33 (6): 2013, 37-40
- [31] Han Shiyan, Li Shujun, Wang Wei, et al. *Preparation of a mesoporous SiO₂ of rosin-based quaternary ammonium salt and CTAB blend template* [J]. *Functional Materials*, 2013, Suppl, 44,126-129.
- [32] Han Shiyan. *Synthesis of rosin-based gemini surfactants and preparation of nanomaterials* [D]. *Northeast Forestry University*, 2012
- [33] Wang Peng. *Study on the synthesis of new mesoporous materials guided by rosin-based quaternary ammonium salts* [J]. *Biomass Chemical Engineering*, 47 (2): 2013
- [34] Zhao Yinfeng. *Synthesis of dehydroabietic amphoteric surfactant and preparation of porous TiO₂* [D]. *Northeast Forestry University*, 2011
- [35] Wang Peng, Zhao Zhendong, Xu Lifeng et al. *Synthesis of highly dispersed fibrous mesoporous γ -Al₂O₃ guided by rosin-based quaternary ammonium salt* [J]. *Forest Products Chemistry and Industry*, 34 (2): 2014, 29-32
- [36] Wang Peng. *Study on the synthesis of new mesoporous materials guided by rosin-based quaternary ammonium salt* [D]. *Chinese Academy of Forestry*, 2012