

POLYSTYRENE SULFONIC ACID RESIN CATALYST, PREPARATION METHOD THEREFOR AND USE THEREOF

TECHNICAL FIELD

5 The present invention relates to a polystyrene sulfonic acid resin catalyst, a preparation method thereof, and the use of the catalyst for separately catalyzing the dehydration of tertiary butyl alcohol and the isobutylene oligomerization to cogenerate isobutylene and diisobutylene.

BACKGROUND ART

10 Isobutylene (IB), particularly IB with high-purity, has a wide range of downstream applications, which relate to many fields such as organic chemical industry, synthetic resin and synthetic rubber etc.

 The dehydration of tertiary butyl alcohol (TBA) is currently one of the mainstream methods for producing isobutylene with high-purity. The dehydration of tertiary butyl alcohol is an
15 endothermic reaction with a heat absorption of 26kJ/mol. The existing dehydrations of tertiary butyl alcohol generally use two processes of reactive distillation and fixed bed. The reactive distillation process needs the TBA in the bottom of the kettle to vaporize constantly to rise to the catalyst bed. Then the IB generated via TBA dehydration under reactive pressure vaporizes and rises to the top of the tower. In order to perform such process, in addition to providing the energy
20 that the reaction needs, large amounts of extra energy should also be provided to compensate the vaporization heat. The fixed-bed process has two types of reactors –multi-stage reactor in series and tubular reactor, wherein the former needs to provide heat between the stages while the later needs to provide heat for the tube pass via the shell pass of the reactor, and the conversion rate per pass is only 31-37% (CN1609082A). In brief, the TBA dehydration process requires the
25 outside to provide a large amount of energy to carry out the reaction.

 The IB oligomerization can be used for producing diisobutylene (2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene)(DIB). The catalysts used in this reaction are generally acidic ion exchange resin and molecular sieve etc. DIB is one of chemical intermediates with extensive uses. It can be used to produce isooctane via hydrogenation. The isooctane is an additive that can be
30 used to increase the gasoline octane number. DIB can also react with phenol to generate octyl phenol, which is further used for producing products such as antioxygen, tackifying resin and surfactant etc. DIB can further be used to produce isononylaldehyde via hydroformylation, and the isononylaldehyde can be used to produce isononanol via hydrogenation and isononanoic acid via oxidation, which is further used to produce products such as plasticizer and lubricating oil etc.

The IB oligomerization is a strong exothermic reaction, which has a heat release up to 107 kJ/mol. And this reaction is a second order reaction, which means that the reaction rate and the exothermal power are directly proportional to the squared concentration of the reactants. Therefore, in such reaction overtemperature is apt to appear in local positions or the position with a higher concentration of IB. The overtemperature in local position is apt to result in high polymerization, isomerism and decomposition of the carbon skeleton, not only leading to the decrease of the dimer-selectivity of C8 alkene, but also leading to the decrease of the concentration of the effective component DIB in the C8 alkene. Therefore, the reaction temperature and the conversion rate per pass should be strictly controlled. It is reported in CN103619785A that when the content of butane in the raw materials is around 85%, even the reaction temperature is 37°C, the dimer-selectivity is only 58% and the content of DIB in the dimers is lower than 93%. The DIB needs to be further purified to reach the market-demanded purity of higher than 95%.

Producing DIB via IB oligomerization also includes two types of processes of reactive distillation and fixed bed.

When DIB is produced via the reactive distillation, the catalysts in the reactive distillation column are stacked bed, which easily leads to an overtemperature in local positions. This would result in on one hand the sharp decrease of the selectivity for DIB, on the other hand the deactivation of the resin catalyst because of the shedding of sulfonic acid groups, while the molecular sieve-like catalysts are easily to be deactivation due to carbon deposition. In the US patents US4242530, US8853483B2 and US20100137668, other hydrocarbons are used to greatly dilute the IB. Although, utilizing the reaction heat, the reactive distillation can provide energy for the vaporization of IB, the energy consumption cannot be significantly decrease because large amounts of diluent are also required to be evaporated and circulated with IB together.

The segment fixed-bed process requires the temperature rise in each stage to be strictly controlled and the heat to be removed by adding heat exchangers between the stages, which makes the entire system need more equipment and investments.

The hot-spot temperature in the tubular fixed-bed oligomerization process is greatly higher than the temperatures of inlet and outlet. In order to strictly control the hot-spot, the IB in the tube pass needs to be diluted with diluents. In US patent US6875900B2, the C4 raw materials contain alkene of C3-C5 or C12 and above as diluents to control the temperature rise. And the shell pass temperature of the tubular reactor must significant lower than the hot-spot temperature to remove the heat quickly, resulting in that except the positions nearby the hot-spots, the temperatures of the other positions in the bed are relatively low and the reaction efficiency decreases as well. In a word, in the traditional tubular fixed-bed process, the IB oligomerization can release a large

amount of heat, which can only be transferred into heat with low quality due to the limits of the reaction temperature and cannot be used efficiently though. And the addition of large amounts of diluent not only reduces the efficiency of the reactor, but also increases the energy consumption for separation.

5 In the prior art, when only performing the IB oligomerization reaction, the raw materials used are all from petroleum cracking. Besides isobutylene, these materials also have components with the reactivity lower than isobutylene, such as propylene, n-butene, propane and butane. Together with oxygen-containing inhibitors, these components control the conversion rate per pass of IB by decreasing the concentration of isobutylene and the reaction rate, so as to increase
10 the selectivity for DIB. How to obtain high per pass conversion of isobutylene and high selectivity of DIB in the absence of other hydrocarbon dilution and inhibitors in the IB oligomerization reactions has not been reported in the currently disclosed techniques. The isobutylene obtained via dehydration almost does not contain other alkene or alkane, and is suitable for using as the starting materials for the IB oligomerization so as to solve the above
15 problems.

Besides, as disclosed in patents CN104447167A, CN1609082A, CN102690159A, CN102485305A and US4423271, the catalysts used in the currently disclosed techniques of the dehydration of tertiary butyl alcohol are mainly focused on polystyrene sulfonic acid resins. Since the dehydration of tertiary butyl alcohol is an endothermic reaction, only by transferring the heat
20 into the inside of the catalyst bed, can the dehydration of tertiary butyl alcohol be assured to react quickly. However, since the heat conduction coefficient of the polystyrene sulfonic acid resin is very poor, it usually results in that the temperature inside the bed is much lower than the outside of the bed. Thus in order to increase the overall efficiency of the catalysts, the temperature outside the bed often needs to be raised. The reaction temperature disclosed in patent US4423271
25 is 80-150°C, wherein a large amount of water generated by the dehydration of tertiary butyl alcohol accelerates the shedding rate of the sulfonic acid in the catalyst, leading to the lifetime of the catalyst no more than 6 months. Thus, if the heat conduction coefficient of the polystyrene sulfonic acid resin catalyst can be raised, there is no need for greatly increasing the temperature outside the bed. The overall catalyst can react in a relatively low temperature and the lifetime
30 would be dramatically prolonged.

The catalysts used in the IB oligomerization include two categories - solid heteropolyacid/activated alumina and macroporous polystyrene sulfonic acid resin, wherein the macroporous polystyrene sulfonic acid resin does not have the problem of carbon deposition. The polymer generated by the oligomerization can all pass through the macropores. But the problem
35 of poor heat-conducting property of the polystyrene sulfonic acid resin also results in that the heat

released is hard to be transferred from the inside of the bed to outside. For such a strong exothermic reaction of isobutylene oligomerization, the bed temperature is relative high because of the heat which often cannot be quickly removed and more C8 isomers are generated in the dimers. Thus the selectivity for DIB and the purity of the products greatly decrease and the catalysts rapidly deactive from the central of the bed. In order to avoid the above problems, in the prior art, in addition to massively diluting the isobutylene, a certain amount of inhibitors such as alcohol, ether or water is required so as to control the conversion rate per pass to be relatively low, which undoubtedly increases the investments for separation and the energy consumption. The heat-conducting properties and the heat-resistance of the activated alumina and solid heteropolyacid are better than the polystyrene sulfonic acid resin. However, as described in the patent CN103619785A, these types of catalysts have the problem of carbon deposition, especially when the raw materials contain a small amount of diene (for example butadiene), thus the catalyst needs to be regenerated frequently.

Thus, there is a need for searching a novel catalyst which can catalyze the dehydration of tertiary butyl alcohol and the isobutylene oligomerization with high efficiency, so as to avoid the disadvantages of heat deactivation of the catalysts, the low concentration of the raw materials and the low selectivity for the products which present in the existing dehydration of tertiary butyl alcohol and the isobutylene oligomerization process due to the insufficient thermal conductivity of the catalysts.

SUMMARY OF THE INVENTION

The object of the present invention is to provide a polystyrene sulfonic acid resin catalyst which contains metal, wherein partly covered by a polystyrene sulfonic acid resin and the metal surface not coated with the polystyrene sulfonic acid resin is converted to sulphate by sulfurization, which effectively improves the thermal conductivity of the resin catalyst, and improves the activity of the catalyst.

Another object of the present invention is to provide a method for preparing the polystyrene sulfonic acid resin catalyst mentioned above.

Yet another object of the present invention is to provide a method for using the polystyrene sulfonic acid resin catalyst separately in the dehydration of tertiary butyl alcohol and the isobutylene oligomerization to cogenerate isobutylene and diisobutylene.

To achieve the above objects, the technical solutions adopted by the present invention are as follows:

A polystyrene sulfonic acid resin catalyst comprising: polystyrene sulfonic acid resin, metal, and metal sulfate, wherein the metal comprises two parts: metal coated with the polystyrene

sulfonic acid resin, and metal not coated with the polystyrene sulfonic acid resin; the metal sulfate is formed by converting the exposed surface of the metal not coated with the polystyrene sulfonic acid resin.

In the catalyst of the present invention, based on the total volume of the metal coated with the polystyrene sulfonic acid resin and the metal not coated with the polystyrene sulfonic acid resin, the proportion of the volume of the metal coated with the polystyrene sulfonic acid resin is 1~90%, preferably 10~70%, more preferably 30~50%; the proportion of the volume of the metal not coated with the polystyrene sulfonic acid resin is 99~10%, preferably 90~30%, more preferably 70~50%.

In the catalyst of the present invention, the metal includes but is not limited to one or more of Fe, Co, Ni, Ge, Sn, Pb, Zn, Cu, Cd, and Sb, preferably one or more of Fe, Co and Ni.

In the catalyst of the present invention, the form of the metal is one or more of metal superfine fiber, foam, and powder; the metal has a minimum dimension size of 0.1~100 μm and a maximum dimension size of less than 2 mm.

The catalyst of the present invention has a particle size of 0.1~3 mm, preferably 0.5~2 mm, a specific surface area of 10-100 m^2/g , a pore size of 10~500 nm, and a pore volume of 0.1~0.5 ml/g.

In the catalyst of the present invention, the volume of the metal coated with the polystyrene sulfonic acid resin accounts for 5~50%, preferably 10~30% of the total volume of the catalyst.

In the catalyst of the present invention, the polystyrene sulfonic acid resin has a number average molecular weight of 50,000 to 200,000, preferably 80,000 to 150,000.

The method for preparing the polystyrene sulfonic acid resin catalyst of the present invention comprises the following steps:

(1) putting the metal into a reaction kettle filled with inert gas, adding a long carbon chain organic compound(s) with polar groups and stirring under the protection of the inert gas, and then leaching out the liquid in the reactor and drying the metal under the atmosphere of inert gas;

(2) adding dibenzoyl peroxide, divinyl benzene, styrene, isopropyl alcohol, and polyvinyl alcohol to the reaction kettle, stirring and heating them up, and adding the metal that has been treated in step (1) to the reaction kettle when a clear phase interface is shown, keeping stirring until the particles obtained begin to become brittle, and then stopping heating and cooling the reaction kettle to room temperature by adding water, leaching out the liquid, and washing and drying the particles;

(3) oxidizing the exposed surface of the metal not coated with polystyrene of the dry particles in the step (2) to obtain metal oxide until the weight of the particles is constant;

(4) heating the particles obtained in the step (3), sulfonating the polystyrene on the surface

of the particles, and converting the metal oxide into metal sulfate to obtain the catalyst.

The preparation process of the catalyst of the present invention is carried out in a stirred reaction kettle with a reflux condenser.

In the preparation method of the catalyst of the present invention, the metal in step (1) is one or more of rust-removed metal fiber, rust-removed metal foam, and rust-removed metal powder, and preferably the rust-removed metal foam. The metal includes but not limited to one or more of Fe, Co, Ni, Ge, Sn, Pb, Zn, Cu, Cd, Sb etc., preferably one or more of Fe, Co, and Ni.

In the catalyst preparation method of the present invention, the inert gas in step (1) is one or more of nitrogen, argon and helium, preferably nitrogen.

In the catalyst preparation method of the present invention, the purpose of adding the long-chain carbon organic compound with polar groups in step (1) is to form a lipophilic layer on the surface of the metal and increase the binding ability of the metal and the polystyrene in the polymerization step. Wherein the long carbon chain organic compound with polar groups is one or more of sulfonates with a general formula of $R-SO_3$, carboxylic acids and their soaps with general formulas of $R-COOH$ and $(R-COO)_nM$ respectively, esters with a general formula of $RCOOR'$, amines with a general formula of $R-NH_2$ and sulfur-nitrogen heterocyclic compounds, preferably esters, wherein R and R' are each a long carbon chain alkyl with carbon number greater than 4, preferably greater than 8; n is an integer of 1~7; the long carbon chain organic compound with polar groups is more preferably one or more of sorbitan monooleate, beeswax, pentaerythritol monooleate, and lanolin; the amount of the long carbon chain organic compound with polar groups is appropriate when its volume is enough to submerge the metal, preferably 1-10 times, more preferably 2-5 times of the volume of the metal.

In the catalyst preparation method of the present invention, step (1) is performed by stirring at room temperature for 0.1~20 hours, preferably 1~10 hours.

In the catalyst preparation method of the present invention, the temperature for drying the metal in step (1) is 50~500°C, preferably 100~200°C.

In the catalyst preparation method of the present invention, the dibenzoyl peroxide is used as an initiator; the divinyl benzene is used as a crosslinking agent; the styrene is used as a polymeric monomer; and the isopropyl alcohol and polyvinyl alcohol are used as cosolvent in step (2).

In the catalyst preparation method of the present invention, the ratio of the total volume of the dibenzoyl peroxide, the divinyl benzene peroxide and the styrene to the volume of the metal in the step (2) is 0.4:1~10:1.

In the catalyst preparation method of the present invention, in step (2), the mass ratio of divinyl benzene to styrene is 1:1-20, preferably 1:5~1:10; the mass ratio of the total mass of the divinyl benzene and styrene to the dibenzoyl peroxide is 20:1~200:1, preferably 50:1~100:1.

In the catalyst preparation method of the present invention, the polyvinyl alcohol in the step (2) is added in the form of an aqueous solution, and the mass content of the polyvinyl alcohol in the polyvinyl alcohol aqueous solution is 0.5~5%, preferably 1~3%; the mass ratio of isopropyl alcohol to polyvinyl alcohol in the polyvinyl alcohol aqueous solution is 5:1~30:1, preferably 10:1~15:1.

In step (2) of the present invention, after the reaction of dibenzoyl peroxide, divinyl benzene, styrene, isopropyl alcohol and polyvinyl alcohol, a suspended polymer is formed, and an obvious phase interface begins to appear between the suspended polymer oil droplets and the solution with the reaction proceeding, and then the metal in step (1) is added.

In the catalyst preparation method of the present invention, the ratio of the total mass of divinyl benzene and styrene to the mass of polyvinyl alcohol aqueous solution in step (2) is 1:3~1:30, preferably 1:5~1:10.

Polystyrene resins with different crosslinking degrees are obtained by controlling the ratio of the styrene to divinyl benzene monomers in step (2), and the number average molecular weight of the polystyrene is controlled to 50,000~200,000, preferably 80,000~150,000. Further, the volume content of the metal in the particles is controlled by controlling the mass ratio of the polystyrene resin to the metal, with reference to the densities of the resins with different crosslinking degrees and the density of the metal.

In the catalyst preparation method of the present invention, the heating process in step (2) is to increase the temperature to 85°C in half an hour. The viscosity and hardness of the particles are monitored during the reaction process. When the particles no longer adhere to each other and become brittle (crush when suffering external force and can no longer undergo plastic deformation), stop heating and cool down the particles to room temperature by adding water to the reaction kettle while stirring. The polyvinyl alcohol and isopropyl alcohol in the surface and pores of the particles are washed out with water after the liquid is leached out, and then the particles are heated to dry the moisture, the drying temperature is 60~110°C, preferably 90~100°C.

In the catalyst preparation method of the present invention, in step (3), the surface of the metal not coated with polystyrene is oxidized by introducing oxygen diluted with inert gas or air diluted with inert gas into the reaction kettle. The volume concentration of oxygen in the oxygen diluted with inert gas or air diluted with inert gas is 0.1~25%, preferably 1~5%. During the oxidation process, the internal temperature of the particle stacks should not exceed 150°C and the oxidation rate is controlled to prevent overtemperature and burning the polystyrene part of the catalyst caused by the metal being oxidized too quickly.

In the catalyst preparation method of the present invention, a sulfur trioxide gas diluted with

inert gas is used to sulfonate the polystyrene on the outer surface of the particles. Specifically, the particles obtained in step (3) are heated to 60~100°C, preferably 70~80°C in a fixed bed for sulfonation, and the sulfur trioxide gas diluted with inert gas, which has been preheated to 60~100°C, preferably 70~80°C, is passed into the fixed bed to sulfonate the particles, wherein the volume concentration of the sulfur trioxide in the sulfur trioxide gas diluted with inert gas is 0.5~10%, preferably 1~5%. The metal oxide not coated with polystyrene on the surface of the particle will be converted into the corresponding metal sulfate, and the polystyrene will be sulfonated to obtain the polystyrene sulfonic acid resin. The particles contain pores; the polystyrene on the outer surface of the particles and the surface of the pores will be sulfonated to obtain the polystyrene sulfonic acid resin. After the sulfonation is completed, the sulfur trioxide is replaced by nitrogen, and the preparation of the catalyst is finished which is then sealed for preservation and kept away from water.

The present invention also provides a method using the above catalyst for catalyzing the dehydration of tertiary butyl alcohol and the isobutylene oligomerization to cogenerate isobutylene and diisobutylene, comprising the following steps:

(1) putting the polystyrene sulfonic acid resin catalyst in the shell pass and tube pass of a tubular reactor separately; and passing the tertiary butyl alcohol which has been preheated into the tube pass of the reactor to perform the dehydration reaction in the presence of the catalyst to generate isobutylene;

(2) separating the isobutylene and tertiary butyl alcohol in the reaction solution obtained in step (1), recycling the tertiary butyl alcohol to the tube pass of the reactor to continue performing the dehydration reaction; and passing all or part of the isobutylene into the shell pass of the reactor to perform the oligomerization reaction in the presence of the catalyst to generate diisobutylene, wherein the isobutylene not passed into the shell pass of the reactor is output as product;

(3) separating the isobutylene and diisobutylene in the reaction solution obtained in step (2), outputting the diisobutylene as product; and recycling all or part of the isobutylene to the shell pass of the reactor to perform the oligomerization reaction, wherein the isobutylene not recycled to the shell pass of the reactor for recycling is output as product.

Alternatively, a method using the catalyst above for catalyzing the dehydration of tertiary butyl alcohol and the isobutylene oligomerization to cogenerate isobutylene and diisobutylene, the method comprises the steps of:

(1) putting the polystyrene sulfonic acid resin catalyst in the shell pass and tube pass of a tubular reactor separately; and passing the tertiary butyl alcohol which has been preheated into the shell pass of the reactor to perform the dehydration reaction in the presence of the catalyst to

generate isobutylene;

(2) separating the isobutylene and tertiary butyl alcohol in the reaction solution obtained in step (1), recycling the tertiary butyl alcohol to the shell pass of the reactor to continue performing the dehydration reaction; and passing all or part of the isobutylene into the tube pass of the reactor to perform the oligomerization reaction in the presence of the catalyst to generate diisobutylene, wherein the isobutylene not passed into the tube pass of the reactor is output as product;

(3) separating the isobutylene and diisobutylene in the reaction solution obtained in step (2); outputting the diisobutylene as product; and recycling all or part of the isobutylene to the tube pass of the reactor to perform the oligomerization reaction, wherein the isobutylene not passed to the tube pass of the reactor for recycling is output as product; The rest is by-product tri- or more isobutylene.

In the present invention, both of the dehydration reaction of tertiary butyl alcohol and the isobutylene oligomerization can be performed in the shell/tube pass and tube/shell pass. The dehydration of tertiary butyl alcohol is an endothermic reaction, and the isobutylene oligomerization is an exothermic reaction. The isobutylene oligomerization and the dehydration of tertiary butyl alcohol are performed in the tube pass and shell pass or performed in shell pass and tube pass of the reactor respectively. Since the heat release of the isobutylene oligomerization is larger than the heat absorption of the dehydration reaction of tertiary butyl alcohol, it is preferable that the dehydration reaction of tertiary butyl alcohol is performed in the shell pass as the cold side, and the isobutylene oligomerization is performed in the tube pass as the hot side. Since the isobutylene oligomerization is a secondary reaction with high exothermic power, the heat transfer distance from the catalyst center to the wall surface can be shortened by performing the oligomerization reaction in the tube pass. Provided that the oligomerization reaction is performed in the shell pass, the distance between the outer walls of the tubes needs to be controlled, for example not exceeding 50 mm, in order to remove the heat in the catalyst bed easily. The separation mentioned in step (2) and step (3) in the method for separately catalyzing the dehydration of tertiary butyl alcohol and the isobutylene oligomerization to cogenerate isobutylene and diisobutylene by using the polystyrene sulfonic acid resin of the present invention may adopt methods known in the art, including but not limited to flash distillation, rectification, and extraction, etc.

In the method for separately catalyzing the dehydration of tertiary butyl alcohol and the isobutylene oligomerization to cogenerate isobutylene and diisobutylene by using the polystyrene sulfonic acid resin of the present invention, the raw material of tertiary butyl alcohol is tertiary butyl alcohol or an aqueous solution of tertiary butyl alcohol, wherein the content of the tertiary

butyl alcohol is 1~100wt%, preferably 30~100wt%, and more preferably 70~100wt%. Since the tertiary butyl alcohol has a relatively high freezing point (24.5°C), the temperature lower than 24.5°C will causes the tertiary butyl alcohol to freeze. Therefore, the raw material for the dehydration of tertiary butyl alcohol must be kept above 24.5°C to make it in a liquid state.

5 However, when the raw material of tertiary butyl alcohol is an aqueous solution, the presence of water will lower the freezing point, and the temperature of the raw material can be appropriately reduced.

In the present invention, in the dehydration of tertiary butyl alcohol, the raw material is fed at top or at bottom. Since the isobutylene formed in the dehydration of tertiary butyl alcohol is a non-polar substance, which shows poor solubility in the polar matter, such as tertiary butyl alcohol and water, and has a lower density than tertiary butyl alcohol and water, and the water in the reaction solution tends to sink as well as the isobutylene tends to rise, thus the tertiary butyl alcohol is preferably fed at top, which can facilitate the discharge of water and make the reaction equilibrium shift to the direction of dehydration.

15 In the present invention, the reaction temperature of the dehydration of tertiary butyl alcohol is 40~200°C, preferably 60~120°C, wherein said reaction temperature is a range between the lowest temperature and the hot-spot temperature in the reactor; the reaction pressure (absolute pressure) is 0.1~10 MPa, preferably 0.2~5 MPa, more preferably 1~4 MPa; and the liquid hourly volume space velocity of the tertiary butyl alcohol is 0.1~50h⁻¹, preferably 0.5~20h⁻¹, more preferably 2~10h⁻¹.

In the present invention, the tertiary butyl alcohol is fed into the reactor in the form of liquid phase with its preheating temperature not exceeding its boiling point under the operating pressure, for example, the boiling point of the tertiary butyl alcohol is 82.5°C under the absolute pressure of 0.1 MPa and the preheating temperature shall not exceed 82.5 °C. The reaction temperature of the isobutylene oligomerization is 30~150°C, preferably 60~110°C, wherein the reaction temperature is a range between the lowest temperature and the hot-spot temperature in the reactor. The isobutylene needs to be fed and reacted in the form of liquid, therefore, its preheating temperature and reaction temperature cannot exceed its boiling point at the corresponding reaction pressure, for example, the preheating temperature and the reaction temperature under an absolute pressure of 2 MPa should be controlled below 100°C. Similarly, when the reaction temperature is determined, the reaction pressure must be maintained above the saturated vapor pressure of isobutylene at the corresponding temperature, for example, at a reaction temperature of 100°C, the reaction pressure must be maintained at an absolute pressure of 2 MPa or more.

35 In the present invention, since the raw material (isobutylene) and products (diisobutylene and triisobutylene) of the isobutylene oligomerization are all non-polar substances and will not

stratify within the bed, therefore, the isobutylene can be fed at top or at bottom.

In the present invention, the reaction temperature of the isobutylene oligomerization is 30~150°C, preferably 60~110°C; the reaction pressure (absolute pressure) is 0.3~20 MPa, preferably 1~10 MPa, more preferably 1~5 MPa; and the liquid hourly volume space velocity of the isobutylene is 1~50h⁻¹, preferably 1~20h⁻¹, more preferably 2~10h⁻¹.

The dehydration reaction of tertiary butyl alcohol is an endothermic reaction, which has the highest temperature and the fastest reaction rate at the inlet of the reactor. As the reaction progresses, the temperature of the bed will gradually decrease, and the reaction rate will also greatly decrease. The isobutylene oligomerization is an exothermic reaction, and as the reaction progresses, the temperature of the bed will gradually increase. If the heat is not removed, the reaction will be out of control, which will increase the content of high polymer and decrease the selectivity of diisobutylene. Therefore, the two reactions-dehydration of tertiary butyl alcohol and isobutylene oligomerization, are separately performed in the shell pass and the tube pass of the tubular reactor, and a feeding manner of co-current is adopted, i.e. both of the tertiary butyl alcohol and isobutylene are fed into the reactor at top, which make the low temperature part of the lower part of the dehydration bed of tertiary butyl alcohol of the shell pass can receive the heat released from the isobutylene oligomerization in the tube pass, the dehydration of tertiary butyl alcohol continue to proceed rapidly, and the temperature rise of the isobutylene oligomerization can be controlled to ensure the selectivity of diisobutylene.

As the polystyrene sulfonic acid resin catalyst which coats the metal is adopted both in the dehydration of tertiary butyl alcohol and the isobutylene oligomerization, its thermal conductivity is greatly improved, so that the heat of isobutylene oligomerization can be quickly transferred from the inside of the tube to the tube wall and further transferred into the inside of the dehydration bed of tertiary butyl alcohol.

The isobutylene oligomerization, in the initial stage, has the highest isobutylene concentration, the fastest reaction rate, and the largest exothermic power. The heat needs to be removed as soon as possible, otherwise a situation of local overtemperature will arise, which leads to the occurrence of high-polymerization, isomerization, and decomposition; and meanwhile accelerates the shedding of the sulfonic acid group and the deactivation of the catalyst. When the catalyst of the present invention is used in the isobutylene oligomerization, since the metal is coated in the polystyrene and the thermal conductivity of the catalyst is greatly improved, the heat generated inside the reactor bed can be rapidly transferred to the outside of the bed, thereby reducing the bed temperature. When the catalyst of the present invention is used in the endothermic dehydration reaction of tertiary butyl alcohol, the heat can also be quickly transferred from the outside of the bed to the inside of the bed.

The dehydration reaction of tertiary butyl alcohol, in the initial stage, has a high concentration of tertiary butyl alcohol, fast reaction rate, and large endothermic power, and needs heat supplement with higher power, especially when a resin catalyst is used. Since the thermal conductivity of the catalyst is low and the heat transfer rate of the catalyst is slow, if the heat cannot be transferred to the inside of the catalyst bed in time, the reaction rate will be greatly reduced. The catalyst of the present invention can transfer the heat from the outside of the bed to the inside of the bed more quickly, so that the reaction proceeds faster.

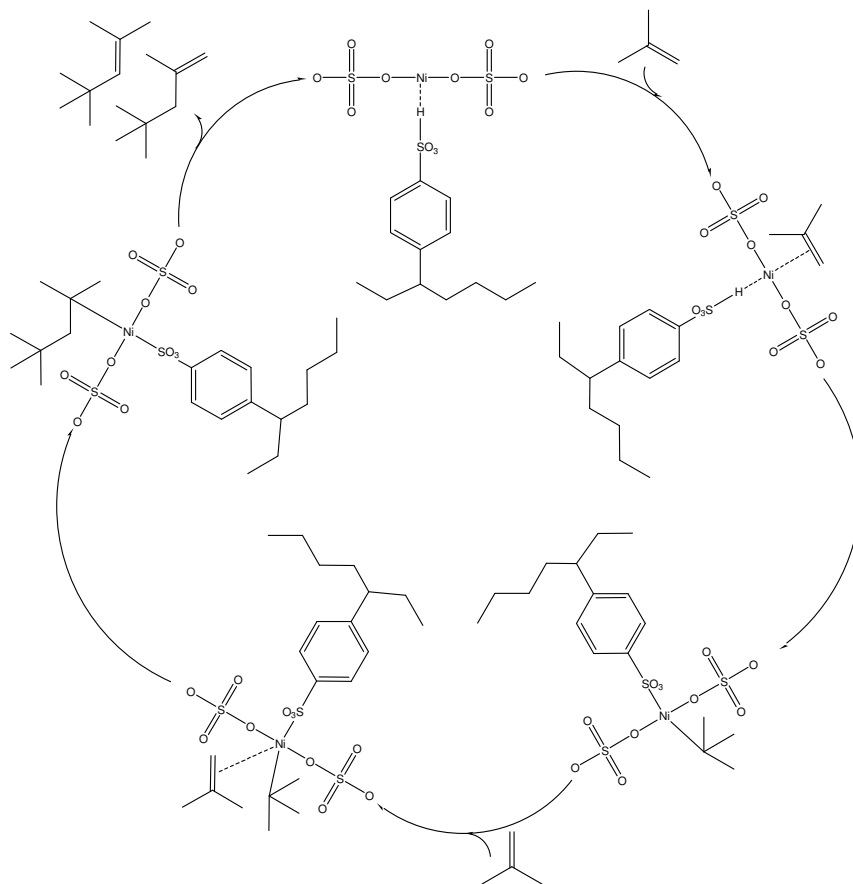
In the present invention, the catalyst is loaded in different sections of the tube pass and shell pass of the reactor in according to the amount of the metal added, the purpose of loading the catalyst in different sections of the bed is that: in the position where the isobutylene oligomerization has the highest reaction rate and the largest exothermic power, the dehydration of tertiary butyl alcohol has the highest reaction rate and the largest endothermic power accordingly, and the catalyst with the highest metal content is loaded at this position, so that the heat released from isobutylene oligomerization can be rapidly transferred to the interior of the dehydration bed of tertiary butyl alcohol, wherein the heat absorption and release of the two reactions are complementary to each other to achieve the purpose of optimizing the bed temperature and reaction effect. For the isobutylene oligomerization reaction; the concentration of isobutylene at the inlet of the bed is the highest; the reaction rate is highest, and the exothermic power is the largest, therefore, the catalyst with the highest metal content is loaded at the inlet of the reactor, so that the heat of the isobutylene oligomerization reaction can be transferred to the outside of the bed in time. The concentration of isobutylene in the middle and rear sections of the bed is gradually decreased. At this time, the bed temperature needs to be maintained to ensure that the reaction can continue, therefore the metal content of the catalyst in the middle and rear sections is gradually decreased. The decreasing of temperature in the inlet section make the conversion rate of isobutylene in the inlet section reduce and more isobutylene react in the middle and rear sections; so that the bed temperature in the middle and rear sections will increase and the temperature in the front and rear sections of the bed tends to be gentle. Similarly, for the dehydration of tertiary butyl alcohol reaction, since the tertiary butyl alcohol concentration at the inlet of the reactor is the highest, the reaction rate is the highest, the endothermic power is the largest, the bed temperature drops rapidly and the heat generated by the isobutylene oligomerization can be conducted to the catalyst bed of the dehydration of tertiary butyl alcohol more rapidly by loading the catalyst with high metal content at the inlet of the bed, which promotes the reaction to proceed faster. As the reaction proceeds, the concentration of tertiary butyl alcohol decreases, the reaction slows down gradually and needs to be provided with heat continuously; and the bed in the middle and rear sections of the isobutylene oligomerization, due

to the increase in temperature, can continuously provide the heat to the dehydration reaction of tertiary butyl alcohol.

In the present invention, the optimization of the bed temperature and heat transfer efficiency allows the temperature of the hot-spot to be greatly reduced, and it is possible to directly use the raw material having an isobutylene content of 80% or more, preferably 90% or more, and more preferably 99% or more, to perform the oligomerization reaction to prepare DIB.

In addition, after the surface of the metal not coated with polystyrene of the catalyst of the present invention is converted to sulfate, the catalyst has the ability of coordination catalysis during the isobutylene oligomerization reaction. Compared with the pure acid catalysis, the coordination catalysis will not result in carbon skeleton isomerization, so that there is almost no useless C8 isomer in the product of isobutylene oligomerization, and the selectivity of DIB is high. When this catalyst is used in the dehydration of tertiary butyl alcohol, due to the presence of a large amount of water in the system, the sulphate is hydrated to lose its catalytic activity. Therefore, when the catalyst of the present invention is used in the dehydration reaction of tertiary butyl alcohol, the metal sulfate does not participate in the catalytic reaction, and the selectivity of isobutylene will not be affected by its high oligomerization catalytic activity. When the catalyst of the present invention is used in the isobutylene oligomerization, due to the large excess of isobutylene, a small amount of water will be hydrated with isobutylene to produce tertiary butyl alcohol and be brought out of the reactor with the product. Therefore, after separating the isobutylene and tertiary butyl alcohol in the reaction solution obtained in step (1) of the present invention, make sure that the water content (mass content) in isobutylene is not higher than 2000 ppm, preferably less than 1000 ppm, more preferably less than 500 ppm.

The specific reaction mechanism of catalyzing the isobutylene oligomerization by the catalyst according to the present invention, exemplified by metal Ni coated in, is as follow: there is a weak interaction between sulfonic acid groups on the polystyrene resin and nickel sulfate, and a Ni-H bond forms between Ni and H; after the coordination of isobutylene with nickel, a hydrogen ion addition reaction occurs; sulfonic acid group and tert-butyl group form a sigma covalent bond directly with nickel; and then another molecule of isobutylene is coordinated with nickel, and a carbon-carbon bond insertion reaction occurs to form an octyl group linked to nickel; and finally a β -hydrogen elimination occurs to form diisobutylene, and the catalyst completes the catalytic cycle.



When the metal sulfate of the catalyst of the present invention hydrates with water during use, which causes partial deactivation of the catalyst, a dehydration regeneration of the catalyst is performed by means of vacuum drying until its weight is no longer reduce, wherein the regeneration temperature is below 150°C, preferably below 110°C.

In the present invention, the raw materials can either be fed to the shell pass of the tubular reactor at top and leave at bottom or vice versa. Feeding in liquid phase at bottom ensures that the entire bed is filled with liquid and is closer to a plug flow, thereby reducing the effect of backmixing. When feeding at top, under the influence of gravity, the liquid will preferentially pass through the flow path with the least resistance, which is easy to form channeling and short circuits: making the residence time distribution in the reactor wider and the temperature distribution more irregular, and resulting in that different tubes have different external temperature distributions, and it is difficult to couple the heat release and absorption between the tube pass and the shell pass. In order to make up for the lack of uneven flow of feeding at top, the general stack bed reactor requires to be equipped with a liquid distributor at the top of the reactor and a redistributor at the middle of the reactor, which increases the difficulty of reactor design and processing.

In the present invention, the height-to-diameter ratio of the tubular reactor is 1~100,

preferably 2~50, more preferably 3~10, and a too low height-to-diameter ratio is unfavorable for uniform distribution of the material flow field in the shell pass. The inner diameter of the tube of the tubular reactor is 3~100mm, preferably 10~60 mm, more preferably 20~50 mm; and the tube is one or a combination of a non-finned tube, inner finned tube, and external finned tube. The use of the inner finned tube or an external finned tube can increase the heat transfer specific surface area. The maximum distance between the outer walls of the tubes is controlled to 3~100 mm, preferably 10~60 mm, more preferably 20~50 mm.

In the present invention, the number of the inlets of the shell pass in the tubular reactor is 1~100, preferably 2~40, and more preferably 4~20. The inlets are evenly distributed along the same horizontal line around the outside of the shell pass of the reactor, or evenly distributed in several groups. For example, there are 20 inlets in total, and they can be evenly distributed with an angle of 9° between them, or they can be divided into 4 groups and each group has 5 inlets, and the angle between the centerlines of the 4 groups is 90° , and the angle between the inlets within one group is less than 9° .

In the present invention, the number of the outlets of the shell pass of the tubular reactor is 1~100, preferably 2~40, and more preferably 4~20. The outlets are evenly distributed along the same horizontal line around the outside of the shell pass of the reactor, or evenly distributed in several groups, for example, there are 20 outlets in total, and they can be evenly distributed with an angle of 9° between them, or they can be divided into 4 groups and each group has 5 outlets, and the angle between the centerlines of the 4 groups is 90° , and the angle between the outlets within one group is less than 9° .

In the present invention, the number of the outlets and the number of the inlets of the shell pass of the tubular reactor may be the same or different; the inlets and outlets are aligned or staggered in the vertical direction, and are preferably staggered. The staggered arrangement of multiple outlets and inlets in the vertical direction can make the fluid distribution of the shell pass more reasonable and minimize dead zones.

In the present invention, the shell pass of the tubular reactor may have baffles or not, and the baffles may be one of a bow shape, a rectangular shape, and a spiral shape, preferably a spiral shape. The baffles having a bow shape and a rectangular shape make the fluid of shell pass flow forth and back on the same plane, while the baffle having a spiral shape can make the fluid of shell pass flow spirally without dead zones, and the distribution of the flow field more even.

The positive effects of the present invention lie in:

The polystyrene sulfonic acid resin catalyst in the present invention can greatly improve the heat conduction of the catalyst in the fixed bed reaction process, and can optimize the temperature distribution of the reaction bed. In the isobutylene oligomerization reaction, the

conversion rate per pass and the product selectivity are greatly improved without the need of significant dilution of the isobutylene.

In addition, the preparation steps of the polystyrene sulfonic acid resin catalyst of the invention are relatively simple, and the morphology and content of each component are easy to
5 characterize.

On the other hand, the present invention solves the problem that the dehydration of tertiary butyl alcohol requires external heat supply while the isobutylene oligomerization requires external heat removal in the reaction of TBA dehydration and isobutylene oligomerization to cogenerate butene and diisobutylene, and reduces the energy consumption of the entire process.

By using the catalyst of the present invention, the conversion rate per pass of the
10 dehydration of tertiary butyl alcohol reaction is over 40%, and the selectivity of isobutylene is over 99%; isobutylene with high concentration can directly be used as a raw material in the isobutylene oligomerization without a large amount of dilution, with the conversion rate per pass of isobutylene over 90%, the selectivity of dimer over 80%, and the DIB content in the dimer
15 over 99%, while no secondary purification is required; the reaction energy consumption of the dehydration of tertiary butyl alcohol and isobutylene oligomerization is reduced and the energy consumption for separation is also reduced.

BREF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic diagram that shows the inlet and outlet settings of the shell pass and
20 the flowing of the shell pass of the tubular reactor;

FIG. 2 is a scanning electron microscope image of Catalyst 1;

FIG. 3 is a scanning electron microscope image after the uncoated metal of Catalyst 1 is
completely dissolved;

FIG. 4 is a schematic diagram of the structure of the catalyst.
25

EMBODIMENTS

The following examples will further illustrate the method provided by the present invention,
30 but the present invention is not limited to the listed examples and should include any other known alternative forms within the scope of the claimed right of the present invention.

Instrument:

Gas Chromatography: Agilent 7890, equipped with a 30m×0.3mm DB-5 capillary column and FID detector; inlet temperature 280°C, heating procedure: keep 50°C for 3min, heat to 300°C
35 by 15°C/min, and keep 300°C for 3min; the detector temperature is 280°C; the carrier gas flow of

argon is 20 ml/min; the flow of hydrogen is 30 ml/min; and the flow of air is 300 ml/min; the split ratio is 10:1.

Scanning electron microscope: JEOL Ltd. JSM-6360LV.

Gel chromatography: (Waters 2410 Refractive Index Detector).

5 Tertiary butyl alcohol, 99.9wt%, Haizheng Chemical Co., Ltd.

Styrene, $\geq 99\%$, Sinopharm Group Chemical Reagent Co., Ltd.

Divinyl benzene, $\geq 99\%$, Aladdin Reagent.

Dibenzoyl peroxide, $\geq 98\%$, Sinopharm Group Chemical Reagent Co., Ltd.

Pentaerythritol monooleate, $\geq 99\%$, Hubei Chushengwei Chemical Co., Ltd.

10 Isopropyl alcohol, $\geq 99\%$, Sinopharm Group Chemical Reagent Co., Ltd.

Test method for the ratio of coated and uncoated metal:

The total volume V1 of the prepared catalyst is measured by the liquid discharge method; then diluted hydrochloric acid of 0.1 mol % is used to slowly dissolve the uncoated metal on the surface of the catalyst, and the digestion degree of the uncoated metal is determined by SEM
15 analysis; after the uncoated metal is completely dissolved (converted to metal chloride and hydrogen), the catalyst is taken out and washed to retest its volume V2;

Tetrahydrofuran is used to dissolve the polystyrene in the catalyst, and the filter residue (remaining metal) is obtained by filtering; and the volume of the filter residue is the volume V3 of the metal coated with polystyrene;

20 The uncoated metal volume is (V1-V2), the total volume of the metal is (V1-V2+V3), and the volume ratio of uncoated metal to the total metal is (V1-V2)/(V1-V2+V3).

Test method for the molecular weight of polystyrene sulfonic acid resin:

The prepared polystyrene sulfonic acid resin is dissolved in tetrahydrofuran, and its number average molecular weight is measured using gel chromatography test.

25

Example 1

The preparation of Catalyst 1:

(1) 323L of rust-removed foam nickel was added to a nitrogen-displaced 1 m³ stirred kettle: the minimum dimension size of the foam nickel is 0.1mm, and the maximum dimension size is
30 0.3mm. 350L of pentaerythritol monooleate was then added to the stirred kettle and stirred at room temperature for 2 hours under the protection of nitrogen. The liquid in the reaction kettle was then leached out through the lower outlet with filter screen under the protection of nitrogen, and the pentaerythritol monooleate on the surface of the foam nickel powder was dried under a nitrogen atmosphere and reserved for further use.

35 (2) 1920 kg of polyvinyl alcohol aqueous solution (1.5 wt%), 288 kg of isopropyl alcohol,

23 kg of divinyl benzene (density: 0.93 kg/L), 68 kg of styrene (density: 0.90 kg/L), 1.8 kg of dibenzoyl peroxide (density: 1.33 kg/L) and 50 L of foam nickel treated in step (1) were added in a 5 m³ stirred kettle with a condensation reflux device. During condensation reflux, the reaction temperature was raised to 85°C within half an hour while stirring, and controlled so that it did not exceed 100°C. The state of the particles was monitored. When the particles began to become brittle, the reactor was removed from the heat and cooled by the cooling coil of the reaction kettle while stirring, and deionized water was added to the reaction kettle to cool it below 30°C. After the liquid was leached out through the lower outlet with filter screen, deionized water was added to wash out the polyethylene and isopropyl alcohol on the surface and in the pores of the particles until the content of isopropyl alcohol in the deionized water of the outlet measured by the gas chromatography was less than 1%.

(3) The particles obtained in step (2) were dried, and then air diluted with an equal volume of nitrogen was slowly introduced to oxidize the outer surface of the foam nickel not coated with polystyrene on the surface of the particles to nickel oxide, during which the internal temperature of the particle stack was kept not higher than 100°C.

(4) The particles prepared in step (3) were placed in a fixed bed and heated to 75°C. A sulfur trioxide gas diluted to 2% with nitrogen was preheated to 75°C and then passed into the above-mentioned fixed bed to convert the nickel oxide not coated with polystyrene on the surface of the particles to nickel sulfate, and the polystyrene was sulfonated to a polystyrene sulfonic acid resin; after the sulfonation was completed, the sulfur trioxide gas was replaced with nitrogen, and the Catalyst 1 prepared was sealed for preservation.

The Catalyst 1 prepared according to the above steps (FIG. 2 is a scanning electron microscope image of the Catalyst 1, and FIG. 3 is a scanning electron microscope image after the uncoated metal in the Catalyst 1 is completely digested) was tested: wherein based on the total volume of foam nickel; the proportion of the foam nickel coated with polystyrene sulfonic acid resin is 70% and the proportion of foam nickel not coated with polystyrene sulfonic acid resin is 30%; the number average molecular weight of the polystyrene resin is 150,000; the average particle size of the Catalyst 1 is 1 mm; the specific surface area is 50 m²/g; the average pore diameter is 300 nm; the pore volume is 0.3 ml/g; and the exchange capacity is 3.5 mol/L. The ratio of the total volume of dibenzoyl peroxide; divinyl benzene and styrene to the volume of metal is 2:1.

Examples 2-4

The preparation of Catalyst 2-4

Except that the ratio of foam nickel to polymer monomers (styrene and divinyl benzene) was

changed, the same method as Example 1 was used. The feeding amount of foam nickel was 50 L, and Catalyst 2-4 were obtained, respectively. See Table 1 for details.

5

Table 1 Catalyst 2-4

Example 2-4	The ratio of the total volume of dibenzoyl peroxide, divinyl benzene and styrene to the volume of metal	The proportion of the coated metal based on the total volume of the metal	The proportion of uncoated metal based on the total volume of the metal	The exchange capacity mol/L
Catalyst 2	0.4:1	10%	90%	1
Catalyst 3	0.7:1	30%	70%	2
Catalyst 4	5:1	40%	60%	3

Examples 5-7

The preparation of Catalyst 5:

Except that the following conditions were changed, the other conditions used in the preparation of Catalyst 5 were the same as in Example 1: the metal was changed to 50L fibrous cobalt with a minimum dimension size of 10 μm , and a maximum dimension size of 30 μm ; the ratio of the total volume of dibenzoyl peroxide, divinyl benzene and styrene to the volume of metal was 10:1; the mass ratio of divinyl benzene to styrene is 1:10; the ratio of the mass of benzoyl peroxide to the total mass of polymeric monomers was 1:100; the mass ratio of isopropyl alcohol to the polyvinyl alcohol in the polyvinyl alcohol aqueous solution (1.5 wt%) was 10:1; and the mass ratio of the total polymeric monomers to the polyvinyl alcohol aqueous solution was 1:30. In the obtained Catalyst 5; the metal coated with the polystyrene sulfonic acid resin accounts for 50% of the total metal volume; the uncoated metal accounts for 50% of the total metal volume; the average particle size of the catalyst is 1 mm; the specific surface area is 10 m^2/g ; the average pore size is 500 nm; the pore volume is 0.1 ml/g; and the exchange capacity is 1.5 mol/L.

Example 6

The preparation of Catalyst 6:

Except that the following conditions were changed, the other conditions used in the preparation of Catalyst 6 were the same as in Example 1: the metal was changed to iron powder with a minimum dimension size of 0.1 μm and a maximum dimension size of 0.2 μm ; the ratio of the total volume of dibenzoyl peroxide, divinyl benzene and styrene to the volume of the metal was 1:2; the mass ratio of divinyl benzene to styrene was 1:7; the mass ratio of dibenzoyl

peroxide to the total polymeric monomers was 1:70; the mass ratio of isopropyl alcohol to the polyvinyl alcohol in the polyvinyl alcohol aqueous solution was 12:1; and the mass ratio of the total polymeric monomers to the polyvinyl alcohol aqueous solution was 1:10. In the obtained Catalyst 6; the metal coated with the polystyrene sulfonic acid resin accounts for 50% of the total metal volume; the uncoated metal accounts for 50% of the total metal volume; the average particle size of the catalyst is 0.5 mm; the specific surface area is 30 m²/g; the average pore size is 100 nm; the pore volume is 0.2 ml/g; and the exchange capacity is 1.5 mol/L.

Example 7

The preparation of Catalyst 7:

Except that the following conditions were changed, the other conditions used in the preparation of Catalyst 7 were the same as in Example 1: the metal was changed to a mixture of foam iron and foam nickel (volume ratio 1: 1) with a minimum dimension size of 10 μm and a maximum dimension size of 2 mm; the ratio of the total volume of dibenzoyl peroxide, divinyl benzene and styrene to the volume of the metal was 1.2:1; the mass ratio of divinyl benzene to styrene was 1:4; the mass ratio of dibenzoyl peroxide to the total polymeric monomers was 1:20; the mass ratio of isopropyl alcohol to the polyvinyl alcohol in the polyvinyl alcohol aqueous solution was 15:1; and the mass ratio of the total polymeric monomers to the polyvinyl alcohol aqueous solution was 1:5. In the obtained Catalyst 7; the metal coated with the polystyrene sulfonic acid resin accounts for 50% of the total metal volume; the uncoated metal accounts for 50% of the total metal volume; the average particle size of the catalyst is 2 mm; the specific surface area is 100 m²/g; the average pore size is 10nm; the pore volume is 0.5 ml/g; and the exchange capacity is 1.5 mol/L.

Examples 8-13

The catalysts 1-7 were evenly loaded in the shell pass and tube pass of the tubular reactor in the order shown in Table 2 below, wherein the TBA dehydration was carried out in the shell pass, the isobutylene oligomerization was carried out in the tube pass, and the reaction conditions and results are shown in Table 2 below. The reactor parameters were as follows: a tubular reactor, tube inner diameter: 40mm, wall thickness: 4mm, the tubes were arranged in an equilateral triangle, tube center spacing: 80mm, tube length: 5m, the number of the tubes: 37; shell pass diameter: 0.56m, the angle between the two inlet axes and the two outlet axes: 90°; and there is no baffle in the shell pass.

Table 2 Reaction Conditions and Results of Examples 8-13

Examples	Reaction Conditions										Reaction Conditions							
	TBA dehydration							DIB					Dehydration of tertiary butyl alcohol		Isobutylene oligomerization			
	Catalyst	Reaction pressure (absolute pressure) MPa	Liquid hourly space velocity of Tertiary butyl alcohol h ⁻¹	Flow of Tertiary butyl alcohol L/h	Inlet temperature °C	Hot-spot temperature °C	Output temperature °C	Catalyst	Reaction pressure (absolute pressure) MPa	Liquid hourly space velocity of Isobutylene h ⁻¹	Flow of Isobutylene L/h	Inlet temperature °C	Hot-spot temperature °C	Output temperature °C	Conversion rate %	Isobutylene selectivity %	DIB Selectivity %	
Example 8	Catalyst 1	2	2	10.57	120	120	98	Catalyst 1	5	2	3.76	90	137	105	69	98.0	99	81
Example 9	Catalyst 2	1.5	3	10.57	100	100	74	Catalyst 1	1.5	3	4.71	50	90	81	61	98.5	90	95
Example 10	Catalyst 2	1	4	10.57	100	100	80	Catalyst 3	4	5	4.24	70	120	89	57	99.0	94	90
Example 11	Catalyst 4	0.5	6	10.57	90	90	74	Catalyst 5	2	7	4.24	70	100	82	53	99.3	92	92
Example 12	Catalyst 6	0.3	8	10.57	80	82	82	Catalyst 7	2.5	9	3.76	90	107	91	46	99.5	95	88
Example 13	Catalyst 7	0.2	10	10.57	60	71	71	Catalyst 1	3	10	3.29	100	113	80	41	99.7	97	85

It can be seen that the conversion rate per pass of TBA in TBA dehydration is above 40%, the selectivity for isobutylene above 98%; the conversion rate per pass of isobutylene in the isobutylene oligomerization is above 90%, and the selectivity for DIB above 80%.

Comparative Example 1

Isobutylene prepared by TBA dehydration reaction.

A tubular reactor, with tube inner diameter: 40mm and wall thickness: 4mm, was used. The tubes were arranged according to an equilateral triangle, wherein the tube center spacing is 80mm, the tube length is 5m, the number of the tubes is 37, the shell pass diameter is 0.56m, the angle between the axe of two inlets and the axe of two outlets is 90°, and there is no baffle in the shell pass. TBA was reacted in the tube pass, the Rohm and Haas Amberlyst-70 Polystyrene resin (Dow Chemical) was loaded with a height of 4.8m. Tertiary butyl alcohol (99.9%) was used as raw material, with the liquid hourly space velocity of 2.0h^{-1} . The inlet temperature of the tertiary butyl alcohol is 80°C, and the pressure is 0.3 MPa. Water at 80°C was fed in from the inlet of the shell pass with a flow rate of $10\text{ m}^3/\text{h}$. The conversion per pass of tertiary butyl alcohol was 21% and the selectivity of IB was 99.9%.

Comparative Example 2

DIB prepared by IB oligomerization.

The reactor was the same as that used in Comparative Example 1. The isobutylene oligomerization was carried out in the tube pass, the Rohm and Haas Amberlyst-70 Polystyrene resin (Dow Chemical) was loaded in the tube pass with a height of 4.8m, the purity of isobutylene was 99.9%, tertiary butyl alcohol was used as a release agent, the content of tertiary butyl alcohol was 5 wt% of isobutylene, the liquid hourly space velocity was 2.0 h^{-1} , the inlet temperature was 80°C, and the pressure was 0.3 MPa. Water at 80°C was fed in from the inlet of the shell pass with a flow rate of $10\text{ m}^3/\text{h}$.

The composition of the materials at the outlet (wt): IB=2.9%, TBA=4.8%, C8=30.1%, C12+=62.3%, DIB content in C8 was 73%, and the others were C8-olefin isomers; the conversion rate per pass was 97%. The temperature in the front section of the catalyst is too high, and the hot-spot reaches 185°C, the reaction temperature was too high and the reaction in the front section was violent, resulting in a large amount of high-polymerization and producing isomers, and the DIB selectivity decreases; Since the isobutylene of front section has been consumed in large quantities, the isobutylene concentration in the latter section has dropped significantly. As a result, the reaction rate in the latter section is very low, the bed temperature is also low, and the catalyst cannot be fully utilized.

Claims

1. A polystyrene sulfonic acid resin catalyst comprising: polystyrene sulfonic acid resin, metal, and metal sulfate, wherein the metal comprises two parts: metal coated with the polystyrene sulfonic acid resin, and metal not coated with the polystyrene sulfonic acid resin; the metal sulfate is formed by converting the exposed surface of the metal not coated with the polystyrene sulfonic acid resin.

2. The catalyst according to claim 1, characterized in that based on the total volume of the metal coated with the polystyrene sulfonic acid resin and the metal not coated with the polystyrene sulfonic acid resin; the proportion of the volume of the metal coated with the polystyrene sulfonic acid resin is 1~90%, preferably 10~70%, more preferably 30~50%; the proportion of the volume of the metal not coated with the polystyrene sulfonic acid resin is 99~10%, preferably 90~30%, more preferably 70~50%.

3. The catalyst according to claim 1 or 2, characterized in that the metal is one or more of Fe, Co, Ni, Ge, Sn, Pb, Zn, Cu, Cd, and Sb, preferably one or more of Fe, Co and Ni; the metal is one or more of metal fiber, foam metal, and metal powder; the metal has a minimum dimension size of 0.1~100 μm and a maximum dimension size of 2 mm or less.

4. The catalyst according to any one of claims 1 to 3, characterized in that the catalyst has a particle size of 0.1~3 mm, preferably 0.5~2 mm, a specific surface area of 10-100 m^2/g , a pore size of 10~500 nm, and a pore volume of 0.1~0.5 ml/g.

5. The catalyst according to any one of claims 1 to 4, characterized in that the polystyrene sulfonic acid resin has a number average molecular weight of 50,000-200,000, preferably 80,000-150,000.

6. A preparation method for the polystyrene sulfonic acid resin catalyst according to any one of claims 1 to 5, the method comprises the steps of:

(1) putting the metal into a reaction kettle filled with inert gas, adding a long carbon chain organic compound with polar groups and stirring under the protection of the inert gas, and then leaching out the liquid in the reactor and drying the metal for standby application under the atmosphere of inert gas;

(2) adding dibenzoyl peroxide, divinyl benzene, styrene, isopropyl alcohol, and polyvinyl alcohol to the reaction kettle, stirring and heating them up, and adding the metal that has been treated in step (1) to the reaction kettle when the reaction shows a clear phase interface, keeping stirring until the particles obtained begin to become brittle, and then stopping heating and cooling the reaction kettle to room temperature by adding water, leaching out the liquid, and washing and drying the obtained particles;

(3) oxidizing the exposed surface of the metal not coated with polystyrene of the dry particles in the step (2) is oxidized to obtain metal oxide until the mass of the particle is constant;

(4) heating the particles obtained in the step (3), sulfonating the polystyrene and converting the metal oxide into metal sulfate to obtain the catalyst is obtained.

7. The preparation method according to claim 6, characterized in that the volume ratio of the total volume of the dibenzoyl peroxide, divinyl benzene and styrene in step (2) to the metal added in step (2) is 0.4:1~10:1.

8. The preparation method according to claim 6 or 7, characterized in that the mass ratio of the divinyl benzene to the styrene in step (2) is 1:1~1:20, preferably 1:5~1:10; the mass ratio of the total mass of the divinyl benzene and styrene to the dibenzoyl peroxide is 20:1~200:1, preferably 50:1~100:1; the polyvinyl alcohol is added in the form of an aqueous solution, the mass ratio of the isopropyl alcohol to the polyvinyl alcohol in the polyvinyl alcohol aqueous solution is 5:1~30:1, preferably 10:1~15:1; the mass ratio of the total mass of the divinyl benzene and styrene to the polyvinyl alcohol aqueous solution is 1:3~1:30, preferably 1:5~1:10.

9. The preparation method according to any one of claims 6 to 8, characterized in that the long carbon chain organic compound with polar groups in step (1) is: one or more of sulfonates with a general formula of $R-SO_3$, carboxylic acids and their soaps with general formulas of $R-COOH$ and $(R-COO)_nM$ respectively, esters with a general formula of $RCOOR'$, amines with a general formula of $R-NH_2$ and sulfur-nitrogen heterocyclic compounds, preferably esters, wherein R and R' are each a long carbon chain alkyl with carbon number greater than 4, preferably greater than 8; n is an integer of 1~7; the long carbon chain organic compound with polar groups is more preferably one or more of sorbitan monooleate, beeswax, pentaerythritol monooleate, and lanolin.

10. A method using the catalyst according to any one of claims 1-5 or the catalyst prepared by the method according to any one of claims 6-9 for separately catalyzing the dehydration of tertiary butyl alcohol and the isobutylene oligomerization to cogenerate isobutylene and diisobutylene, the method comprises the steps of:

5 (1) putting the polystyrene sulfonic acid resin catalyst in the shell pass and tube pass of a tubular reactor separately; and passing the tertiary butyl alcohol which has been preheated into the tube pass of the reactor to perform the dehydration reaction in the presence of the catalyst to generate isobutylene;

10 (2) separating the isobutylene and tertiary butyl alcohol in the reaction solution obtained in step (1), recycling the tertiary butyl alcohol to the tube pass of the reactor to continue performing the dehydration reaction; and passing all or part of the isobutylene into the shell pass of the reactor to perform the oligomerization reaction in the presence of the catalyst to generate diisobutylene, wherein the isobutylene not passed into the shell pass of the reactor is output as product;

15 (3) separating the isobutylene and diisobutylene in the reaction solution obtained in step (2), and outputting the diisobutylene is output as product; recycling all or part of the isobutylene to the shell pass of the reactor to perform the oligomerization reaction, wherein the isobutylene not passed to the shell pass of the reactor for recycling is output as product;

or,

20 (1) putting the polystyrene sulfonic acid resin catalyst in the shell pass and tube pass of a tubular reactor separately; and passing the tertiary butyl alcohol which has been preheated into the shell pass of the reactor to perform the dehydration reaction in the presence of the catalyst to generate isobutylene;

25 (2) separating the isobutylene and tertiary butyl alcohol in the reaction solution obtained in step (1), recycling the tertiary butyl alcohol to the shell pass of the reactor to continue performing the dehydration reaction; and passing all or part of the isobutylene into the tube pass of the reactor to perform the oligomerization reaction in the presence of the catalyst to generate diisobutylene, wherein the isobutylene not passed into the tube pass of the reactor is output as product;

30 (3) separating the isobutylene and diisobutylene in the reaction solution obtained in step (2); outputting the diisobutylene as product; and recycling all or part of the isobutylene to the tube pass of the reactor to perform the oligomerization reaction, wherein the isobutylene not passed to the tube pass of the reactor for recycling is output as product.

11. The method according to claim 10, characterized in that the temperature of the dehydration reaction of the tertiary butyl alcohol is 40-200 °C, preferably 60-120 °C; the absolute pressure of the reaction is 0.1~10 MPa, preferably 0.2~5 MPa, more preferably 1~4 MPa; the liquid hourly space velocity of the tertiary butyl alcohol is 0.1~50h⁻¹, preferably 0.5~20h⁻¹, more preferably 2~10h⁻¹; and the temperature of the isobutylene oligomerization reaction is 30~150°C, preferably 60~110°C; the absolute pressure is 0.3~20MPa, preferably 1~10MPa, more preferably 1~5MPa; and the liquid hourly volume space velocity of the isobutylene is 1~50h⁻¹, preferably 1~20h⁻¹, more preferably 2~10h⁻¹.