

PROCESS FOR FRAGMENTING A SHAPED ARTICLE OF ZEOLITE

BACKGROUND OF THE INVENTION

Field of the Invention

5 The present invention relates to a process for fragmenting a shaped article of zeolite, for example, a shaped article of zeolite which had been used as a catalyst for the Beckmann rearrangement reaction.

10 Description of the Related Art

 There have been conventionally known processes comprising carrying out the Beckmann rearrangement reaction of cyclohexanone oxime in a gas phase in the presence of a solid catalyst as one of the production processes of ϵ -caprolactam
15 (for example, refer to EP 0380364). As the catalyst, zeolites such as crystalline silica and crystalline metallosilicate are useful and are usually used in the form of pellets or fine particles (for example, refer to EP 0576295). Usually, with the lapse of time, the catalyst lowers its activity due to the precipitation
20 of a carbonaceous substance, thermal degradation and the like, therefore, there proposed various regeneration processes such as calcination, chemical treatment and the like (for example, refer to EP 0388070, Japanese Patent Application Laid-open No. 2003-236394 and No. 5-170732, and EP 1352902).

25 When repeating regeneration and reuse of the

above-mentioned shaped article of zeolite as a catalyst, the properties of the shaped article, for example, pore volume, bulk density, strength and the like, fluctuate; therefore, stable operation is hardly carried out and stable reaction results are hardly obtained. Consequently, in order to restore the properties, it is desirable that the shaped article of zeolite which has been repeating regeneration and reuse to a certain degree is to be fragmented and shaped again. As the process for fragmenting such a shaped article, physical processes such as a dry process by a hammer mill, a jet mill and the like, and a wet process by a ball mill, an Atrigher and the like, are usually adopted. However, when the shaped article of zeolite is fragmented by such physical processes, crystallinity may be lowered, fragmenting may not be adequate and zeolite suitable for shaping again may not be occasionally obtained. Accordingly, it is an object of the present invention to provide a process for effectively fragmenting a shaped article of zeolite with suppressing the lowering of crystallinity.

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SUMMARY OF THE INVENTION

The present invention provides a process for fragmenting a shaped article of zeolite, comprising a step of contacting a shaped article of zeolite with an aqueous basic solution containing at least 2% by weight of quaternary ammonium.

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According to the present invention, the shaped article

of zeolite can be efficiently fragmented with suppressing the lowering of crystallinity.

DETAILED DESCRIPTION OF THE PREFERRED EXAMPLES

5 The process for fragmenting of the present invention is applied to a shaped article of zeolite, particularly a shaped article of pentasyl type zeolite, especially a shaped article of MFI type zeolite. The zeolite is a porous crystalline material containing silicon and oxygen as elements for composing its
10 skeleton, and may be a crystalline silica whose skeleton is substantially composed of only silicon and oxygen or may be crystalline metallosilicates and the like containing besides other elements as elements for composing the skeleton. In case of the crystalline metallosilicates and the like, examples of
15 the element capable of existing other than silicon and oxygen include Be, B, Al, Ti, V, Cr, Fe, Co, Ni, Cu, Zn, Ga, Ge, Zr, Nb, Sb, La, Hf, Bi and the like, and mixtures containing 2 or more of these elements may be used if necessary. Zeolite can be preferably produced by hydrothermal synthesis of a silicon
20 compound, if necessary together with a template agent, a metal compound and the like.

 The shape of the shaped article of zeolite is selected in accordance with its use, and the shaping method is selected in accordance with the shape. For example, when it is used as
25 a catalyst for a fixed bed reaction, a shaped article whose shape

is columnar or cylindrical pellet is advantageously produced by extrusion molding or compression molding. Further, when it is used as a catalyst for a fluidized bed reaction or a moving bed reaction, a shaped article whose shape is spherical fine
5 particle is advantageously produced by a spray drying of slurry.

As the zeolite to be shaped, those having a primary particle diameter of 5 μm or less usually and 1 μm or less preferably are used. Further, a binder may be used at shaping, if necessary. Further, when treatment such as calcination and activation is
10 carried out, it may be carried out before shaping or after shaping, or may be carried out at both of before shaping and after shaping.

As described above, when the shaped article of zeolite is used, for example, as a catalyst for the Beckmann rearrangement reaction of cyclohexanone oxime, its activity is lowered with
15 the lapse of time; therefore, regeneration processing is carried out at appropriate timing. When regeneration and reuse are thus repeated, it may become difficult to continue operation or to maintain the performance of reaction because of the property's fluctuation of the shaped article of zeolite; therefore, in
20 order to restore the properties, it is desirable that the shaped article of zeolite which has been repeating regeneration and reuse to a certain degree is to be fragmented and shaped again. Thus in the present invention, the shaped article of zeolite, which is usually an already-used catalyst, is contacted with
25 aqueous basic solution containing quaternary ammonium in order

to be fragmented. By adopting such a treatment, the lowering of crystallinity of zeolite can be suppressed, effective fragmenting can be carried out and zeolite suitable for re-shaping can be advantageously obtained.

5 The above-mentioned aqueous basic solution can be typically prepared by dissolving quaternary ammonium hydroxide which is a basic substance containing quaternary ammonium, in water. Further, the solution may be prepared by dissolving quaternary ammonium salts such as the chloride, bromide, sulfate
10 or nitrate of quaternary ammonium and a basic substance other than quaternary ammonium hydroxide in water. Further, as the component to be dissolved, a quaternary ammonium hydroxide and a basic substance other than the quaternary ammonium hydroxide may be used together or a quaternary ammonium hydroxide and a
15 quaternary ammonium salt may be used together.

Typical examples of the quaternary ammonium contained in the above-mentioned aqueous basic solution can be indicated by the following formula (1).



20 wherein each of R^1 , R^2 , R^3 and R^4 represents an alkyl group, an aralkyl group, an aryl group or an allyl group.

In the formula (1), when at least one of R^1 , R^2 , R^3 and R^4 is an alkyl group, its carbon number is usually about 1 to about 4, and examples of the alkyl group include a methyl group,
25 an ethyl group, a propyl group, a butyl group and the like. When

at least one of R^1 , R^2 , R^3 and R^4 is an aralkyl group, its carbon number is usually about 7 to about 10, and examples of the aralkyl group include a benzyl group, a tolylmethyl group and the like. When at least one of R^1 , R^2 , R^3 and R^4 is an aryl group, its carbon
5 number is usually about 6 to about 10, and examples of the aryl group include a phenyl group, a tolyl group and the like.

Examples of the quaternary ammonium indicated by the formula (1) include tetramethylammonium, tetraethylammonium, n-propyltrimethylammonium, tetra-n-propylammonium,
10 tetra-n-butylammonium, benzyltrimethylammonium, dibenzyltrimethylammonium, trimethyladamantylammonium and the like. Further, examples of the quaternary ammonium other than the compounds indicated by the formula (1) include 4,4'-trimethylenebis(dimethylpiperidinium),
15 1,1'-butylenebis(4-aza-1-azoniabicyclo[2,2,2]octane), and the like. Among these, tetraalkylammonium is preferable.

Further, examples of the basic substance other than the quaternary ammonium hydroxide which may be used for preparation of the above-mentioned aqueous basic solution include ammonia,
20 primary amines, secondary amines, tertiary amines, metal hydroxides such as sodium hydroxide and potassium hydroxide, etc.

The concentration of quaternary ammonium in the above-mentioned aqueous basic solution is at least 2% by weight
25 and preferably 4% by weight or more. When the concentration

of quaternary ammonium is too low, the shaped article may hardly be fragmented. Further, the upper limit of the concentration of quaternary ammonium is suitably adjusted but is usually up to 40% by weight.

5 Further, pH of the above-mentioned aqueous basic solution is usually 10 or more and preferably 11 to 14. When pH is too low, the shaped article of zeolite may be hardly fragmented.

 The contacting of the shaped article of zeolite with the above-mentioned aqueous basic solution can be preferably carried
10 out by immersing and stirring the shaped article of zeolite in the above-mentioned aqueous basic solution in a stirring vessel. Further, the contacting may be carried out in a batch-wise type and may be carried out in a continuous type. The contacting temperature is usually 50 to 250°C, preferably 50 to 170°C and
15 more preferably 60 to 120°C and the contacting time is usually 0.1 to 100 hours. Further, the amount of the above-mentioned aqueous basic solution used is usually 80 to 5000 parts by weight based on 100 parts by weight of the shaped article of zeolite.

 A particularly preferred embodiment of the present
20 invention is that a spherical fine particle comprising plural primary particles of zeolite is contacted with above-mentioned aqueous basic solution to be fragmented and to yield primary particles of zeolite. More preferably, the spherical fine particle may be a used catalyst, especially a used catalyst that
25 has already been used more than one time for the Beckmann

rearrangement reaction of cyclohexanone oxime.

The slurry of zeolite which is obtained by fragmenting the shaped article of zeolite, in the above-mentioned aqueous basic solution, is subjected to a re-shaping process; or is
5 subjected to a treatment such as concentration, dilution, filtration, rinsing or drying, and then, is subjected to a re-shaping process. Further, the re-shaping process may be carried out by mixing the slurry with new zeolite or its slurry.

10 Examples

Example of the present invention is shown below, but the present invention is not limited thereto. In Examples, the measurement of the average particle diameter and X-ray diffraction intensity of a catalyst or crystal were carried out
15 by methods below.

[Average particle diameter]

A diameter of 50% by volume (volume median diameter) was measured using a particle size distribution measurement device ["MICROTRAC HRA Model 9320-X100" manufactured by Nikkiso Co.,
20 Ltd.] and this was referred to as the average particle diameter.

[X-ray diffraction intensity]

It was measured using Copper K α -beam as a light source, using an X-ray diffraction device ["RINT-2100V" manufactured by Rigaku Corporation].

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Reference Example 1 (Gas phase Beckmann rearrangement reaction)

A shaped article of zeolite (secondary particle) having an average particle diameter of 60 μm was used as a catalyst, which shaped article of zeolite was spherically shaped from zeolite (primary particle) having an average particle diameter of 0.2 μm which is composed of crystalline silica having an MFI structure. In a fluidized bed reactor in which the catalyst was fluidized, reaction was carried out at 380°C for 3 months by feeding vaporized cyclohexanone oxime, methanol and nitrogen gas, and extracting reaction product gas. During the reaction, the space velocity WHSV [feed speed (g/h) for catalyst weight (g)] of cyclohexanone oxime was 2 h^{-1} and the feed proportion of cyclohexanone oxime/methanol/nitrogen gas was 1 kg/1.8 kg/0.3 m^3 . Further, during the reaction, a portion of the catalyst was extracted from the reactor, introduced into a calcinator, calcined at 500°C under air flow for a residential time of 20 hours, and introduced again into the reactor thereby circulating the catalyst between the reactor and the calcinator.

Water was added to the used catalyst obtained to prepare slurry of 5% by weight, the average particle diameter of the used catalyst was measured and as a result, it was 56.3 μm . Further, the X-ray diffraction intensity of the used catalyst was measured, an MFI structure was established and the peak intensity of $2\theta = 23^\circ$ was referred to as a basis value (100%) in the following.

Example 1

300 g of the used catalyst obtained in Reference Example 1 was charged in a beaker, 700 g of a 6% by weight aqueous tetra-n-propylammonium hydroxide solution (the concentration of tetra-n-propylammonium is 5.5% by weight; pH = 13) was added thereto, and the mixture was stirred at 110°C for 6 hours. Water was added to the slurry obtained to prepare a 5% by weight slurry, and the average particle diameter was measured to be 0.2 μm .

Further, the slurry was filtrated, and crystals remaining after filtration were dried, then calcined at 530°C under nitrogen flow for 1 hour and calcined at 530°C under air flow for 1 hour to obtain powdery white crystals. When the X-ray diffraction intensity of the powdery white crystals was measured, an MFI structure was established and the peak intensity of $2\theta = 23^\circ$ was 126% against the same peak intensity of the used catalyst obtained in Reference Example 1.

Comparative Example 1

1000 g of the used catalyst obtained in Reference Example 1 was charged in a plastic tank and 1500 g of pure water was added thereto to prepare a 30% by weight slurry. The slurry was fed to a ball mill at a rate of 300 ml/min to grind the catalyst. Water was added to the slurry obtained to prepare a 5% by weight slurry, and the average particle diameter was measured to be

2.0 μm .

Further, the slurry was filtrated and crystals remaining after filtration were dried, then calcined at 530°C under nitrogen flow for 1 hour and calcined at 530°C under air flow for 1 hour
5 to obtain powdery white crystals. When the X-ray diffraction intensity of the powdery white crystals was measured, an MFI structure was established and the peak intensity of $2\theta = 23^{\circ}$ was 87% against the same peak intensity of the used catalyst obtained in Reference Example 1.

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WHAT IS CLAIMED IS:

1. A process for fragmenting a shaped article of zeolite,
comprising a step of contacting a shaped article of zeolite with
5 an aqueous basic solution containing at least 2% by weight of
quaternary ammonium.

2. The process according to Claim 1, wherein the shaped
article of zeolite is a shaped article of pentasyl type zeolite.

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3. The process according to Claim 1 or 2, wherein the
quaternary ammonium is a tetraalkylammonium.

4. The process according to any one of Claims 1 to 3,
15 wherein the shaped article of zeolite is the one which had been
used as a catalyst for the Beckmann rearrangement reaction of
cyclohexanone oxime.