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(54) Title: ALUMINOSILICATE CATALYST FOR PREPARATION PROPYLENE VIA METHANOL

(57) Abrégé/Abstract:
A process for the preparation of P-HZSM-5 for methanol conversion to light olefins especially propylene, with utilizing a tetraalkylphosphonium salt, is disclosed. The catalyst based on crystalline aluminosilicates of the pentasil type, having an $SiO_2/A1_2O_3$ molar ratio at least 280, the BET surface area from 300 to 400 m^2/g, total pore volume at least 0.15 and at most 0.4 cm^3/g, the average pore diameter at least 2 and at most 20 nm and mean crystallites size at least 1 and at most 11 μm.

ALUMINOSILICATE CATALYST FOR PREPARATION PROPYLENE VIA METHANOL

Abstract

A process for the preparation of P-HZSM-5 for methanol conversion to light olefins especially propylene, with utilizing a tetraalkylphosphonium salt, is disclosed. The catalyst based on crystalline aluminosilicates of the pentasil type, having an SiO_2/Al_2O_3 molar ratio at least 280, the BET surface area from 300 to 400 m^2/g, total pore volume at least 0.15 and at most 0.4 cm^3/g, the average pore diameter at least 2 and at most 20 nm and mean crystallites size at least 1 and at most 11 μm.

Background of the invention

Zeolite molecular sieve catalysts are one of the most versatile catalysts ever found in this technology. Zeolite is three-dimensional, crystalline compounds, which are built from AlO_4 and SiO_4 tetrahedral. It exhibits such properties as being a shape-selective catalyst with unusual catalytic properties, high thermal stability and high quality of ion-exchanging, so that, zeolites have dedicated numerous technical applications, for example they are used as sorbents, ion-exchangers, separation medias and pollution control agents in the petroleum, chemical and process industries.

Catalysts based on crystalline aluminosilicates which are prepared from a source of aluminum, a source of silicon, a source of alkali, a template and water, Depending on the composition of the starting mixture, the size of the primary crystallites is 1 micron or less. Commercially important zeolites, such as ZSM-5 and beta, can be produced under "hydrothermal" conditions, in which a silicon source, an aluminum source, optionally an organic template and a mineralizer (for example, alkali metal hydroxides or fluorides or HF) were converted at more than 100° C. under pressure in the pH range between 4 and 14. Hydrothermal syntheses of zeolites with a Si/Al atomic ratio of more than 20, for example, pentasil, are run in autoclaves at temperatures that are

generally higher than 130° C., for example, at 180.degree (Accordance with U.S. Pat. No. 3,702,886, U.S. Pat. No. 6645461 and U.S. Pat. No. 6054113).
Methanol conversion is one of the promising and indirect processes in reducing natural gas resources to valuable products such as polymers. In which, the methanol-to-olefins conversion is noticeable process by scientists in recent years which is performed on an acidic molecular sieve catalyst bed.

Production of methanol conversion catalysts based on crystalline aluminosilicates is known from DE-A-28 22 725. The diameter of the primary crystallites is 1 μm and more. According to West German Patent No. DE 2,405,909, the catalysts for hydrocarbon conversion are prepared on the basis of zeolites of the ZSM-5 type, the mean diameters of the primary crystallites being in the range from 0.05 to 0.1 micron.

According to DE-A-29 35 123. ZSM-5 or ZSM-11 zeolites are prepared, using ammonium hydroxide and an alcohol as template, in which the presence of nuclei is characteristic. The zeolites are used as cracking and hydrocracking catalysts and as catalysts for isomerization and dewaxing.

A method for production of large flat-structured crystals of zeolites of the pentasil type from SiO_2 and a compound of one or more trivalent elements, like Al, B, Fe, Ga, Cr, in amine-containing solutions is known from DE-A-35 37 459, characterized by the fact that highly dispersed SiO_2, prepared by burning of a silicon chloride compound, is used as starting material. The zeolites are used for conversion of organic compounds, especially for conversion of methanol to hydrocarbons containing lower olefins and aromatics. The obtained zeolites are not agglomerated.

European Patent No. EP-123,449 describes a process for converting alcohol or ethers into olefins, using steam-treated zeolite catalysts; the latter have a crystal size of less than 1 micron and can be incorporated into a matrix. Clays, silica and/or metal oxides are mentioned as matrix materials.

EP 0 362 364 A1 concerns catalysts based on crystalline aluminosilicates of the pentasil type with an Si/Al atomic ratio of at least 10, constructed from primary crystallites with an average diameter of at least 0.1μ.m and, at most, 0.9 μ.m. The size of the primary crystallites is considered important for the lifetime of the catalyst. The same applies for EP 0 448 000 A1.

U.S. Pat. No. 4,206,085 relates to hydrocarbon conversion catalysts based on zeolites and a matrix material, for increasing the abrasion resistance. The matrix material used is alumina from pseudoboehmite, and SiO_2 from ammonium polysilicate or silica sol. The preferred zeolite is of the faujasite type. There are no data on the size of the zeolite crystals.

U.S. Pat. No. 5063187 concerns catalyst based on crystalline aluminosilicates of the pentasil type, having an Si/Al atomic ratio of at least 10, has the structure of primary crystallites of a mean diameter of at least 0.1 micron and at most 0.9 micron.

According to U.S. Pat. No. 0138053 A1 concerns a method for conversion of methanol to olefins, using zeolites catalysts based on crystalline aluminosilicates the pentasil type, characterized by the fact that it is constructed from primary crystallizes with an average diameter of at least 0.01 μm and less than 0.1 μm, that are combined to at least 20% to agglomerates. The catalyst which was used for a method for conversion of methanol to olefins, especially propylene, has an Si/Al atomic ratio of about 50 to 250, preferably about 50 to 150, especially about 75 to 120, or the catalyst for an olefin to olefin conversion, has an Si/Al atomic ratio between 10 and 100, preferably between about 20 and 65, especially about 20 and 50.

Summary of the invention

The present invention relates to catalysts based on crystalline aluminosilicate of the pentasil type having a SiO_2/Al_2O_3 molar ratio at least 280. These catalysts have an increased activity and selectivity in methanol

conversion process to light olefins, in particular in methanol conversion to propylene (MTP).

These catalysts are defined by a structure of crystallites of a mean diameter of at least about 1 μm and at most 11 μm, the BET surface area from 300 about to 400 m^2/g, total pore volume about to 0.15 to about 0.4cm^3/g and the average pore diameter at least 2 and at most 20 nm.

These catalysts were prepared from a source of aluminum, silicic acid as a source of silicon and tetraalkylphosphonium compounds (for example Tetra-n-butylphosphonium bromide) as a source of template.

Detailed description of the Invention

In the catalyst of this invention, the crystallites have a mean diameter of at least about 1 micron and at most 11 micron. Preferably, the mean diameter of the crystallites is in the range from 4 to 8 micron. The pure catalyst (without binder) determines the BET surface area from 300 to 400m^2/g, the total pore volume between 0.15 and 0.4 cm^3/g, and the pore diameter have preferably, a diameter of 2-20 nm.

The catalyst according to the invention is obtainable preferably in the following manner:

(a) In an aqueous reaction batch containing a source of aluminum, sodium hydroxide, a source of tetraalkylphosphonium template, and a source of silicon alumimosilicate gel is produced at room temperature and converted to a crystalline aluminosilicate under hydrothermal condition in a sealed tube.

(b) The crystallites are separated from the aqueous reaction medium, dried, washed with ionized water and subjected to an appropriate calcination process.

(c) The product from stage (b) is reacted in an aqueous medium with an ammonium salt on heating in a manner that described in U.S. Pat. No. 4,

447,669 for the purpose of exchanging the sodium ions with hydrogen ions.

(d) The product from stage (c) is mixed with an amorphous silica -alumina binder; and

(e) The product from stage (d) is subjected to a final calcination.

The catalyst according to the invention is obtainable is explained in more detail below:

In stage (a), an aqueous reaction batch containing a source of silicon (for example silicic acid), a source of aluminum (for example sodium aluminate), sodium hydroxide and a template of tetraalkylphosphonium compound (for example tetra-n-butylphosphonium bromide) is first prepared. The proportions by weight between the source of silicon and the source are aluminum are selected such that the crystalline aluminosilicates having an SiO_2/Al_2O_3 mole ratio of at least 200, preferably of about 300 to about 400, are obtained. An alkaline alumimosilicate gel (synthesis gel) is produced from the reaction batch at room temperature and is transformed to alumimosilicate crystallites under an elevated temperature from 150 to 190° C under hydrothermal condition in an autoclave fitted with a polytetrafluoroethylene (PTFE) inner lining for a duration from 1 to 8 days.

The templates used are tetraalkylphosphonium compounds, wherein each alkyl group contains 4 carbon atoms. Preferred templates are tetra-n-butylphosphonium bromide (TnBPBr), chloride, and hydroxide. The aqueous reaction batch of stage (a) has preferably by a pH value from 10.5 to 13.5.

In stage (b) the product crystallites are separated in a manner that described in U.S. Pat. No. 5,063,187.

The intermediate calcination can be completed in an oxidizing atmosphere at about 500 to 550° C.

In stage (c) the product from stage (b) is reacted in an aqueous medium with ammonium nitrate on heating in a manner that described in U.S. Pat. No. 4,

447,669. The Na form of zeolite is added to 1M solution of ammonium nitrate. The mixture is stirred at a temperature 60° C for 4 hours. The product is recovered by filtration. This operation is renewed third times. The product is then dried and then calcined in air at 650° C for 3 hours.

In stage (d) the product from stage (c) is mixed with the amorphous alumimosilicate binder composed 65% of Al_2O_3 and 35% of SiO_2 in a manner that described in U.S. Pat. No. 4,616,098. The extrudates are dried at 110° C for 16 hours and calcined at 550° C for 12 hours.

The end product thus obtained can be used in methanol conversion processes for the production of light olefins, especially for propylene.

EXAMPLE 1

This example illustrates the preparation of zeolite ZSM-5. 9.625 grams $NaAlO_2$ (comp.: 53 wt. percent Al_2O_3, 44.5 wt. percent Na_2O, 2.5 wt. percent H_2O) partially dissolved in 5400 ml. 0.067 N sodium hydroxide by vigorous stirring. There was slowly added 339.35 grams of tetra-n-butylphosphonium bromide as a template. 966.00 grams silicic acid ($SiO_2.0.5H_2O$) was added to above mixture under vigorous stirring at about 500 rpm. After about 90 minutes with stirring, the pH of reaction mixture was adjusted about 10.3 value by sulfuric acid addition. The resulted mixture had the following composition: 15.00 mole SiO_2, 0.050 mol Al_2O_3, 0.250 mole Na_2O, 1.000 mole $(CH_3CH_2CH_2CH_2)_4PBr$, 80 mole H_2O. The mixture was placed in a PTFE lined autoclave and heated at 190° C for 24 hours with stirring about 200 rpm. The resultant solid product was cooled to room temperature, removed, washed with 80 liter H_2O. The product was then dried overnight at 105° C. A portion of this product was subjected to X-ray analysis and identified ZSM-5 phase accompanied by amorphous. The product was then calcined in air at 550° C for 10 hours.

Example 2

This example illustrates the preparation of zeolite ZSM-5. 9.625 grams $NaAlO_2$ (comp.: 53 wt. percent Al_2O_3, 44.5 wt. percent Na_2O, 2.5 wt. percent H_2O) partially dissolved in 7200 ml. 0.050 N sodium hydroxide by vigorous stirring. There was slowly added 339.350 grams of tetra-n-butylphosphonium bromide as a template. 1380 grams silicic acid ($SiO_2.0.5H_2O$) was added to above mixture under vigorous stirring at about 500 rpm. After about 90 minutes with stirring, the pH of reaction mixture was adjusted about 10.3 value by sulfuric acid addition. The resulted mixture had the following composition: 20.00 mole SiO_2, 0.050 mol Al_2O_3, 0.250 mole Na_2O, 1.00 mole $(CH_3CH_2CH_2CH_2)_4PBr$, 400 mole H_2O. The mixture was placed in a PTFE lined autoclave and heated at 190° C for 96 hours with stirring about 200 rpm. The resultant solid product was cooled to room temperature, removed, washed with 80 liter H_2O. The product was then dried overnight at 105° C. A portion of this product was subjected to X-ray analysis and identified pure-phase ZSM-5 that had a degree of crystallinity of 100%, the BET surface area $325m^2/g$, total pore volume 0.20 cm^3/g, the average pore diameter from 2 to 20 nm and crystallite size 4-8 μm.

The product was then calcined in air at 550° C for 10 hours. The analysis results of product are indicated in table I.

Example 3:

This example illustrates the preparation of zeolite ZSM-5. 9.625 grams $NaAlO_2$ (comp.: 53 wt. percent Al_2O_3, 44.5 wt. percent Na_2O, 2.5 wt. percent H_2O) partially dissolved in 9000 ml. 0.040 N sodium hydroxide by vigorous stirring. There was slowly added 335.350 grams of tetra-n-butylphosphonium bromide as a template. 1725 grams silicic acid ($SiO_2.0.5H_2O$) was added to above mixture under vigorous stirring at about 500 rpm. After about 90 minutes with stirring, the pH of reaction mixture was adjusted about 10.3 value by sulfuric acid addition. The resulted mixture had the following composition: 25.00 mole SiO_2, 0.050 mol Al_2O_3, 0.040 mole Na_2O, 0.198 mole $(CH_3CH_2CH_2CH_2)_4PBr$, 80 mole H_2O. The mixture was placed in a PTFE lined autoclave and heated at

190° C for 192 hours with stirring about 200 rpm. The resultant solid product was cooled to room temperature, removed, washed with 80 liter H_2O. The product was then dried overnight at 105° C. A portion of this product was subjected to X-ray analysis and identified 25 wt. percent of ZSM-5 phase and 75 wt. of alpha-quartz phase. The product was then calcined in air at 550° C for 10 hours. The analysis results of product are indicated in table I.

TABLE I

	Example		
	1	2	3
Time (h)	24	96	192
Temperature (°C)	190	190	190
Reaction composition, moles			
SiO_2	280	400	500
Al_2O_3	1	1	1
Na_2O	5	5	5
$(CH_3CH_2CH_2CH_2)_4PBr$	20	20	20
Product, weight percent in the H-form zeolite (calcined 550°C)			
Na_2O	0.076	0.071	0.051
Al_2O_3	0.545	0.453	0.341
P_2O_3	0.199	0.153	0.168
SiO_2	99.34	99.52	99.41
Total as oxides	100.16	100.20	99.97
SiO_2/Al_2O3	309.87	373.47	495.59
Na_2O/Al_2O_3	0.229	0.258	0.246
P_2O_3/Al_2O_3	0.339	0.313	0.457
Product phase(s)	ZSM-5 + Amorphous	Pure ZSM-5	25%ZSM-5 + 75% Quartz

Application Example:

The catalyst conversion of methanol to light olefins especially propylene over P-HZSM-5 catalyst (Catalyst of example 2) with SiO_2/Al_2O_3 molar ratio of 373 was performed in a fixed-bed stainless steel reactor (1 inch I.D.). For methanol conversion, 300 grams of shaped catalyst was placed between two beds of alumina balls with the same dimension of the catalyst. Prior to introducing methanol feed, the catalyst was heated under flow of nitrogen (300 ml/min) at 550°C during 12 hours. Typical test of catalyst was experienced in condition of a pressure of 1atm. (1.04 bar),

temperature of 460-480°C, WHSV of $1h^{-1}$, with a feed of 50% methanol in water. The conversion of methanol was defined as:

$$X = \frac{n^{\circ}CH_3OH - (nCH_3OH + 2nDME)}{n^{\circ}CH_3OH} \times 100\%$$

Wherein X is the conversion, $n^{\circ}CH_3OH$ is the moles of methanol fed to the reactor per unit time, nCH_3OH is the moles of unreacted methanol leaving the reactor per unit time, nDME is the moles of dimethyl ether leaving the reactor per unit time. That is, the moles of dimethyl ether are treated as equivalent moles to unreacted methanol, not as a reaction product. Distribution of hydrocarbons and oxygen products are shown in table II.

TABLE II

TOS(h)	24	36	48	60	72	90
Product Distribution (mole %)						
C_1-C_4 Paraffin	8.03	8.81	8.21	7.87	7.73	7.64
C_2-C_4 Olefin	72.78	77.30	73.33	70.52	69.95	69.56
C_5+ Gasoline	18.09	9.79	16.62	17.27	20.10	18.08
Oxygenates	1.10	4.09	1.85	4.34	2.22	4.72
Total	100.00	100.00	100.00	100.00	100.00	100.00
C_2 Olefin	19.90	19.54	17.81	15.68	14.86	13.85
C_3 Olefin	37.04	40.65	39.85	39.38	40.19	40.42
C_3 Olefin/C_2 Olefin	1.86	2.08	2.24	2.51	2.70	2.92
%Conversion (CH_3OH)	99.79	99.85	99.61	99.10	99.59	98.85

References

1. J. Robert and US Patent 3,702,886 (1972).
2. K. Unger, US Patent 6,645,461 (2003).
3. D. Vaughan, US Patent 6,054,113 (2000).
4. Change, European Patent Application, EP-A-123 449 (1984).
5. European Patent Application, EP 0362 364 A1.
6. M. Schneder, European Patent Application, EP 0 448 000 A1 (1991).
7. J. Lim, US Patent 4,206,085 (1980).
8. G. Burgfels, US Patent 5,063,197 (1991).

What is claimed is:

1. A crystalline aluminosilicate zeolite catalyst used for converting methanol to light olefins, wherein the crystalline aluminosilicate zeolite catalyst comprises molar ratios of the oxides $xNa_2O:Al_2O_3:yP_2O_3:zSiO_2$, and wherein:

x ranges from 0.2 to 0.4,

y ranges from 0.3 to 0.5,

z is greater than or equal to 280,

the average diameter of the crystalline aluminosilicate zeolite catalyst ranges from 1 μm to 11 μm, and

the BET surface area of the crystalline aluminosilicate zeolite catalyst ranges from 300 m^2/g to 400 m^2/g.

2. The crystalline aluminosilicate zeolite catalyst according to claim 1, wherein z ranges from 300 to 500.

3. The crystalline aluminosilicate zeolite catalyst according to claim 1 or claim 2, wherein z ranges from 300 to 450.

4. The crystalline aluminosilicate zeolite catalyst according to any one of claims 1 to 3, wherein z ranges from 350 to 400.

5. The crystalline aluminosilicate zeolite catalyst according to any one of claims 1 to 4, wherein a template is used to prepare the crystalline aluminosilicate zeolite catalyst, the template being tetra-n-butylphosphonium salt TnBPM, wherein M is Cl, Br, or OH.

6. The crystalline aluminosilicate zeolite catalyst according to any one claims 1 to 5, wherein the average diameter of the crystalline aluminosilicate zeolite catalyst ranges from 1 μm to 11 μm.

7. The crystalline aluminosilicate zeolite catalyst according to any one of claims 1 to 6, wherein the average diameter of the crystalline aluminosilicate zeolite catalyst ranges from 4 μm to 8 μm.

8. The crystalline aluminosilicate zeolite catalyst according to any one of claims 1 to 7, wherein the total pore volume of the crystalline aluminosilicate zeolite catalyst ranges from 0.15 cm^3/g to 0.4 cm^3/g.

9. The crystalline aluminosilicate zeolite catalyst according to any one of claims 1 to 8, wherein the crystalline aluminosilicate zeolite catalyst is calcined at a temperature ranging from 500°C to 800°C for 6 hours to 28 hours to prepare the crystalline aluminosilicate zeolite catalyst.

10. The crystalline aluminosilicate zeolite catalyst according to any one of claims 1 to 9, wherein the pore diameter of the crystalline aluminosilicate zeolite catalyst ranges from 2 nm to 20 nm.