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(54) Benævnelse: **ZEOLIT Y**

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Fortsættes ...

DESCRIPTION

[0001] The present invention relates to modified zeolite Y and to a process for preparing such a modified zeolite Y.

[0002] Zeolite Y is a well-known zeolite form and has a wide range of documented uses as catalyst supports, adsorbents, selective separation materials, etc. in the petrochemical and chemical industries and also as pollution control materials for industrial, domestic and automotive use. Zeolite Y, for example, is one of the main zeolitic materials proposed for hydrocracking use. Early findings showed that modification of the basic materials described in US-A-3,130,007 to produce a lowering of the unit cell size, gave improved selectivity to the desired middle distillate, or mid-barrel, products.

[0003] It has now surprisingly been found that a specific kind of zeolite Y easily can be treated to obtain zeolite Y having modified properties. It was found possible to reduce the acidity of zeolite Y thereby.

[0004] Accordingly, the present invention provides a process for preparing a modified zeolite Y which process comprises subjecting zeolite Y having a silica to alumina molar ratio of at least 10 and a unit cell size less than 24.40 Å to calcination at a temperature of from 700 to 1000 °C wherein (i) the steam partial pressure is at most 0.06 bar at a temperature of from 700 to 800 °C, (ii) the steam partial pressure is at most 0.08 bar at a temperature of from greater than 800 to 850 °C, (iii) the steam partial pressure is at least 0.03 bar at a temperature of from 850 to less than 900 °C, and (iv) the steam partial pressure is at least 0.05 bar at a temperature of from 900 to less than 950 °C and (v) the steam partial pressure is at least 0.07 bar at a temperature of from 950 to 1000 °C. Furthermore, also described is a zeolite Y obtainable by such process.

[0005] WO-A-2004/047988 discloses a hydrocracking catalyst composition comprising an optional metal hydrogenation component supported on a carrier comprising a zeolite of the faujasite structure.

[0006] Prior art documents such as WO-A-2004/047988 and WO-A-2005/084799 describe a broad temperature range as being suitable for calcining zeolite Y in combination with binder. However, someone skilled in the art would be aware that the majority of such range is not suitable as a high temperature is suspected of breaking down the zeolitic structure. Therefore, someone skilled in the art would not seriously contemplate to apply the full temperature range of 300 to 800 °C mentioned in WO-A-2004/047988 or 300 to 850 °C mentioned in WO-A-2005/084799 but would only consider a relatively narrow range around the calcination temperature actually applied, i.e. 535 °C.

[0007] Further, it was found that modified zeolite Y obtainable by the process of the present invention, differ from known zeolite Y in their infrared spectrum. Therefore, the present invention further relates to a modified zeolite Y having a silica to alumina molar ratio of at least 10, the infrared spectrum of which has a peak at 3700 cm^{-1} but substantially no peak at 3670 cm^{-1}, and optionally substantially no peak at 3605 cm^{-1}.

[0008] Furthermore, it was found that a specific kind of acidity of the zeolite Y modified by the present invention is less than the acidity of known zeolite Y. Therefore, the present invention also relates to a modified zeolite Y having a silica to alumina molar ratio of at least 10, the infrared spectrum of which has a peak at 3700 cm^{-1} but substantially no peak at 3670 cm^{-1}, and optionally substantially no peak at 3605 cm^{-1} and wherein the modified zeolite Y has an acidity as measured by exchange with perdeuterated benzene of at most 20 micromole/gram, optionally at most 10 micromole/gram.

[0009] The calcination of the zeolite Y is carried out at a temperature of from 700 to 1000 °C. The time during which the zeolite Y is calcined influences the exact temperature to be applied. Generally, the temperature is at most 850 °C. At a calcination temperature of more than 900 °C, loss of crystallinity was observed. The time during which the zeolite Y is calcined preferably is of from 20 minutes to 5 hours, more preferably of from 30 minutes to 4 hours. The time period to be applied depends on whether the oven is preheated or whether the temperature is increased while the catalyst carrier is being calcined. The time period preferably is at least 40 minutes, more preferably at least 50 minutes. Further, the time period is preferably less than 4 hours, more preferably less than 3 ½ hours. The temperature preferably is at most 850 °C, more preferably at most 820 °C, most preferably at most 800 °C.

[0010] The calcination of the zeolite Y is carried out in the presence of steam. The steam partial pressure preferably is at most 0.04 bar at a temperature of from 700 to 800 °C. The steam partial pressure preferably is at most 0.07 bar at a temperature of from 800 to 850 °C. The steam partial pressure preferably is at least 0.05 bar, more specifically at least 0.07 bar at a temperature of from 850 to 900 °C. The steam partial pressure preferably is at least 0.07 bar at a temperature of from 900 to 950 °C. The steam partial pressure preferably is at least 0.08 bar, more specifically at least 0.1 at a temperature of from 950 to 1000 °C. The steam partial pressure preferably is at most 0.5 bar, more specifically at most 0.4 bar. Also described is calcination carried out in the absence of steam.

[0011] It is preferred that the zeolite Y is calcined in the absence of amorphous binder.

[0012] Preferred zeolite Y materials for use in the present invention are zeolite Y having a silica to alumina ratio (SAR) of more than 10, especially an ultrastable zeolite Y (USY) or a very ultrastable zeolite Y (VUSY) of unit cell size (a_0) less than 2.440 nm (24.40 Angstroms), in particular less than 2.435 nm (24.35 Angstroms) and a SAR of more than 10, specifically of more than 10 up to 100. Suitable zeolite Y materials are known, for example, from European Patent Specifications Nos. 247 678 and 247 679, and WO 2004/047988.

[0013] Whilst USY and VUSY Y zeolites are preferred for use in the present invention, other Y zeolite forms are also suitable for use, for example the known ultrahydrophobic Y zeolites.

[0014] VUSY zeolite of EP-A-247 678 or EP-A-247 679 is characterised by a unit cell size below 2.445 nm (24.45 Angstroms) or 2.435 nm (24.35 Angstroms), a water adsorption capacity (at 25 °C and a p/p_0 value of 0.2) of at least 8 %wt of the zeolite and a pore volume of at least 0.25 ml/g wherein between 10% and 60% of the total pore volume is made up of pores having a diameter of at least 8 nm.

[0015] Most preferred are the low unit cell size, high surface area zeolite Y materials described in WO-A-2004/050548. Such materials can be described as a zeolite Y having a SAR of greater than 13, a unit cell size in the range of from 24.10 (2.410 nm) to 24.40 Å (2.440 nm), and a surface area of at least 875 m^2/g as measured by the BET method and ATSM D 4365-95 with nitrogen adsorption at a p/po values of 0.02, 0.03 and 0.04. Said materials can be prepared by a process which comprises

1. a) providing a starting zeolite of the faujasite structure having a silica to alumina ratio of from 4.5 to 6.5 and an alkali level of less than 1.5%wt;
2. b) hydrothermally treating said starting zeolite at a temperature in the range of from 600 to 850 °C, preferably 600 to 700 °C more preferably 620 to 680 °C and especially 630 to 670 °C, and at a partial pressure of, preferably externally supplied, steam in the range of from 0.2 to 1 atmosphere for a time effective to produce an intermediate zeolite having a unit cell size of from 24.30 to 24.45 Å, being suitably in the range of from 0.5 to 5 hours, more suitably 1 to 3 hours;
3. c) contacting the intermediate zeolite with an acidified solution comprising an acid and optionally an ammonium salt under conditions effective to produce a high surface area zeolite having a unit cell size in the range of from 24.10 to 24.40 Å, a molar bulk silica to alumina ratio of greater than 13 and a surface area of at least 875 m^2/g, thereby producing the high surface area zeolite; and
4. d) recovering the high surface area zeolite.

[0016] Especially preferred high surface area materials
have one or more of the following features:

unit cell size in the range of from 24.14 to 24.38, preferably from 24.24, more preferably from 24.30, to 24.38, preferably to 24.36, especially to 24.35 Å, and specifically in the range of from 24.14 to 24.33 Å;

a SAR in the range of from 20 to 100, preferably from 20 to 80, especially to 50;

surface area of at least 890, specifically at least 910 m^2/g;

a micropore volume,as determined by nitrogen porosimetry using the t-plot method, also known as the t-method, using nitrogen as the adsorbate as described by Lippens, Linsen and de Boer, Journal of Catalysis, 3-32,(1964), of greater than 0.28 ml/g, suitably greater than 0.30 ml/g. Generally micropore volume will be less than 0.40 ml/g, suitably less than 0.35 ml/g. Herein micropores are pores having a diameter of less than 2 nm.

[0017] The present invention also relates to a modified zeolite Y wherein the modified zeolite Y has an acidity as measured by exchange with perdeuterated benzene of at most 20 micromole/gram. This acidity more preferably is at most 15, more preferably at most 12, more preferably at most 10 and most preferably at most 8 micromole/gram.

[0018] The zeolites of the present invention find particular use as adsorbents, showing versatility in the type of material that can be absorbed. Adsorption capability even at low partial pressure of adsorbate has been found for both polar and non-polar materials. This makes the zeolites of the present invention very attractive for general adsorbency use and for use in pollution control. As polar materials, water and polar hydrocarbons may be mentioned. As non-polar materials, non-polar hydrocarbons, such as aromatic hydrocarbons, for example benzene and toluene, may be mentioned. Accordingly, the present invention also provides for use as adsorbents of the modified zeolites Y according to the present invention, especially the zeolites Y of reduced acidity.

[0019] The present invention will now be illustrated by the following Examples.

Examples

[0020] In the Examples the following test methods have been used:

Unit cell size: Determined by X-ray diffraction using the method of ASTM D-3942-80.

Surface Area: Determined in accordance with the conventional BET (Brunauer-Emmett-Teller) method nitrogen adsorption technique as described in the literature at S. Brunauer, P. Emmett and E. Teller, J. Am. Chm. Soc., 60, 309 (1938), and ASTM method D4365-95. In the determinations quoted below, the results are given as a single point assessment taken at a nitrogen partial pressure of 0.03 following a high temperature pretreatment. (see also note below).

Silica to alumina molar ratio (SAR): Determined by chemical analysis; values quoted are 'bulk' SAR (that is to say the overall SAR) and not specifically the SAR of the crystalline framework.

Zeolite Y preparation

[0021] The zeolite Y utilised in the catalysts of the present invention was prepared in accordance with the teaching of WO 2004/047988. The starting material used was low alkali content (<1.5 %wt alkali oxide) ammonium form Y zeolites. These zeolites were prepared by one of two methods known in the art. While not meaning to be exclusive of other methods of achieving similar results, the examples were prepared by either the Cooper method (as described in U.S. patent specification No. 5,435,987) which involves K^+ ion exchange of Na form zeolite Y, followed by ammonium ion exchange, or by the Alafandi method (as described in U.S. patent specification No. 4,085,069) which involves ammonium exchange under autogenous superatmospheric pressure. The low alkali content ammonium form Y zeolite was steam calcined in one or two steps to create an ultrastable type Y zeolite. The steamed zeolites were then subjected to an acid-dealumination treatment consisting of a one step treatment with a combination of ammonium chloride and hydrochloric acid. The water content in the ion-exchange-dealumination treatment was generally sufficient to provide a zeolite slurry with from 5 to 25% anhydrous zeolite. Such variation is not believed to materially affect the results obtained.

[0022] The zeolite Y obtained had a silica to alumina molar ratio of 25, a unit cell size of 24.33 A and a surface area of 922 m^2/g.

Infrared spectrum

[0023] Additionally, the IR spectrums of the above catalyst carriers were measured with the help of a Biorad FTS175 FT-IR spectrometer using a mercury cadmium telluride detector. The cell is equipped with a sample holder comprising 10 positions and samples have been measured as self-supporting wafers with a diameter of 18 mm, pressed from 25.3 +/- 0.1 mg zeolite powder at 24 - 28 MPa (3.5 - 4 Ton pressure). For the background measurement an open position of the sample holder has been used. Background and sample spectra have been measured by collecting 250 scans at 2 cm^{-1} resolution. The spectrometer is flushed with nitrogen to minimize the interference of water vapor. After evacuating to less than $5x10^{-4}$ mbar, samples have been activated in situ in a special heating zone by applying a temperature program of ramping to 450 °C at a rate of 10 °C/min, with a hold time of 30 minutes at 450 °C. Subsequently, samples have been cooled to 50 °C with 20 °C/min. Then background and sample IR spectra have been measured.

H/D acidity

[0024] After recording the above-mentioned spectra, the sample holder is slid back to the heating zone, and equilibrated at 50 °C for an additional 15 min, while the vacuum is maintained. H/D exchange has been performed in situ by letting 8-9 Torr (1.07 - 1.2 kPa) of hexadeuterobenzene (C_6D_6) interact with the activated zeolite samples for 15 min at 50°C followed by evacuation for 45 minutes to a target pressure of $5x10^{-4}$ mbar (with a maximum of 1 hour). Then background and sample IR spectra have been measured.

[0025] To quantify the total amount of acidity, the IR spectra of the sample before (OH spectrum) and after (OD spectrum) contact with hexadeuterobenzene were compared as follows. The obtained OH spectrum was subtracted from the OD spectrum and baseline corrected. Then curve-fitting was performed with a predefined peak set for VUSY type materials and previously determined extinction coefficients.

Crystallinity

[0026] The crystallinity is measured by comparing with a highly crystalline VUSY reference by following the changes in peak broadening measured by XRD.

Example 1

[0027] Table 1 shows the properties of a sample of zeolite Y prepared as described above which has been calcined for 2 hours at 600 °C.

Table 1

Reference 1	
Unit cell size (nm)	2.433
Crystallinity (%)	99
SAR	24.95
HD acidity (micromole/gram)	175

[0028] Further samples of the freshly prepared zeolite Y also were calcined during 2 hours but now in the presence of steam and at a higher temperature as described in Table 2. The properties of the thus calcined zeolite Y are also shown in this Table.

Table 2

	Reference 1	Sample 1	Sample 2
Calcination T (°C)	600	900	950
Steam (bar partial pressure)	na	0.1	0.1
Surface Area (m^2/g)	929	816	804
Micropore Volume (cc/g)	0.310	0.278	0.274
Mesopore Volume (cc/g)	0.186	0.189	0.192

[0029] The IR spectrums of the zeolite Y samples were measured as described above. It was found that samples 1 and 2 had a peak at 3700 cm^{-1} but substantially no peaks at 3605 and 3670 cm^{-1}. The IR spectrum of Reference 1 was the opposite, i.e. it had peaks at 3605 and 3670 cm^{-1} and no peak at 3700 cm^{-1}.

(i) Example 2

[0030] In a similar fashion to Example 1, Table 3 shows the properties of a sample of zeolite Y prepared as described above and having been calcined for 2 hours at 600 °C.

Table 3

Reference 2	
Unit cell size (nm)	2.432
Crystallinity (%)	88
SAR	28.72
HD acidity (micromole/gram)	209

[0031] Further samples of the freshly prepared zeolite Y also were calcined during 2 hours in the absence of steam and at a higher temperature as described in Table 4. The properties of the thus calcined zeolite Y are also shown in this Table.

Table 4

	Reference 2	Sample 3
Calcination T (°C)	600	850
Surface Area (m^2/g)	859	834
Micropore Volume (cc/g)	0.284	0.274
Mesopore Volume (cc/g)	0.159	0.176

[0032] The IR spectrums of the zeolite Y samples were measured as described above. It was found that Sample 3 had a peak at 3700 cm^{-1} but substantially no peaks at 3605 and 3670 cm^{-1}. The IR spectrum of Reference 2 was the opposite, i.e. it had peaks at 3605 and 3670 cm^{-1} and no peak at 3700 cm^{-1}.

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

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ZEOLIT Y

PATENTKRAV

1. Fremgangsmåde til fremstilling af en modificeret zeolit Y, hvilken fremgangsmåde omfatter udsættelse af zeolit Y med et forhold mellem siliciumdioxid og aluminiumoxid på mindst 10 og en enhedscellestørrelse, der er mindre end 24,40 Å, for kalcinering ved en temperatur på fra 700 til 1000 °C, hvor (i) damppartialtrykket er højest 0,06 bar ved en temperatur på fra 700 til 800 °C, (ii) damppartialtrykket er højest 0,08 bar ved en temperatur på fra højere end 800 til 850 °C, (iii) damppartialtrykket er mindst 0,03 bar ved en temperatur på 850 til lavere end 900 °C, og (iv) damppartialtrykket er mindst 0,05 bar ved en temperatur på fra 900 til lavere end 950 °C og (v) damppartialtrykket er mindst 0,07 bar ved en temperatur på fra 950 til 1000 °C.

2. Fremgangsmåde ifølge krav 1, i hvilken fremgangsmåde den modificerede zeolit Y har et molforhold mellem siliciumdioxid og aluminiumoxid på mere end 10.

3. Fremgangsmåde ifølge krav 1 eller krav 2, i hvilken fremgangsmåde kalcineringen udføres i et tidsrum på fra 20 minutter til 5 timer.

4. Fremgangsmåde ifølge et hvilket som helst foregående krav, i hvilken fremgangsmåde zeolit Y før kalcinering har et molforhold mellem siliciumdioxid og aluminiumoxid i bulk på mere end 13, en enhedscellestørrelse i intervallet på fra 24,10 til 24,40 Å, og et overfladeareal på mindst 875 m^2/g målt ved hjælp af BET-metoden og ATSM D 4365-95 med nitrogenadsorption ved p/po-værdier på 0,02, 0,03 og 0,04.

5. Modificeret zeolit Y med et molforhold mellem siliciumdioxid og aluminiumoxid på mindst 10, hvis infrarøde spektrum har et peak ved 3700 cm^{-1} men i alt væsentligt intet peak ved 3670 cm^{-1}, og eventuelt i alt væsentligt intet peak ved 3605 cm^{-1}.

6. Modificeret zeolit Y ifølge krav 5, hvor den modificerede zeolit Y har en surhed målt ved udveksling med perdeutereret benzen på højest 20 mikromol/gram, eventuelt højest 10 mikromol/gram.

7. Fremgangsmåde til anvendelse af en zeolit, hvor den modificerede zeolit Y ifølge et hvilket som helst af kravene 5 til 6 anvendes som et adsorberende stof.

8. Anvendelse af en modificeret zeolit Y ifølge et hvilket som helst af kravene 5 til 6 som et adsorberende stof for både polare og ikke-polare materialer.

9. Anvendelse ifølge krav 8 til anvendelse i bekæmpelse af forurening.