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(54) Title: DEALUMINIZED CATALYST SUPPORT, METHOD FOR PRODUCING SAID CATALYST SUPPORT AND METHOD FOR HYDRATING C_2- OR C_3-OLEFINS WITH WATER IN THE PRESENCE OF A CATALYST CONSISTING OF THIS CATALYST SUPPORT IMPREGNATED WITH ACID

(54) Bezeichnung: ENTALUMINIERTER KATALYSATORTRÄGER, VERFAHREN ZUR HERSTELLUNG DES KATALYSATORTRÄGERS UND VERFAHREN ZUR HYDRATISIERUNG VON C_2- ODER C_3-OLEFINEN MIT WASSER IN GEGENWART EINES KATALYSATORS, DER AUS DIESEM MIT SÄURE GETRÄNKTEN KATALYSATORTRÄGER BESTEHT

(57) Abstract

The invention relates to a dealuminized catalyst support, to a method for producing a catalyst support with a reduced aluminium content based on naturally occurring sheet silicates, for example montmorillonite, and to a method for hydrating C_2- or C_3-olefins using the catalyst support with the reduced aluminium content. The support is impregnated with phosphoric acid for the acid-catalysed hydration reaction. The invention improves on conventional hydration methods since no aluminium can leach out of the support in the presence of the phosphoric acid. As a result, there are no longer any aluminium phosphate blockages to be expected in the apparatus connected downstream of the reaction.

(57) Zusammenfassung

Beansprucht wird ein entaluminierter Katalysatorträger, ein Verfahren zur Herstellung eines Katalysatorträgers mit verringertem Aluminiumgehalt auf Basis natürlich vorkommender Schichtsilikate, wie beispielsweise Montmorillonit sowie ein Verfahren zur Hydratisierung von C_2- oder C_3-Olefinen, bei welcher der Katalysatorträger mit verringertem Aluminiumgehalt eingesetzt wird. Für die sauer katalisierte Hydratisierungsreaktion wird der Träger mit Phosphorsäure getränkt. Die erfindungsgemässe Verbesserung gegenüber dem herkömmlichen Hydratisierungsverfahren besteht darin, daß keine Aluminium-Auslaugung des Trägers in Gegenwart der Phosphorsäure mehr stattfinden kann. Somit sind in den der Reaktion nachgeschalteten Apparaten keine Verblockungen durch Aluminiumphosphat mehr zu erwarten.

Summary

Dealuminated catalyst carrier, process for producing the catalyst carrier and process for hydrating C_2 or C_3 olefins with water in the presence of a catalyst which comprises this catalyst carrier impregnated with acid.

What is claimed is a dealuminated catalyst carrier, a process for producing a catalyst carrier with reduced aluminium content based on naturally occurring lattice-layer silicates, such as for example montmorillonite, as well as a process for the hydration reaction of C_2 or C_3 olefins in which said catalyst carrier with reduced aluminium content is used. For acid-catalysed hydration reaction the catalyst carrier is impregnated with phosphoric acid.

The improvements according to the invention of the hydration reaction compared to conventional processes include the fact that no aluminium is leached out of the carrier in the presence of the phosphoric acid. As a result no more blockage of the succeeding apparatusdue to aluminium phosphate are expected.

Dealuminated catalyst carrier, process for producing the catalyst carrier and process for hydrating C_2 or C_3 olefins with water in the presence of a catalyst which consists of this catalyst carrier impregnated with acid.

This invention relates to a dealuminated catalyst carrier, a process for producing catalyst carrier and a process for hydrating C_2 or C_3 olefins with water in the presence of a catalyst which comprises this catalyst carrier impregnated with acid.

It is known that olefins of low molecular mass which are linear or have only few branches can be converted to alcohols by a reaction with steam in the gas phase under the application of high temperatures and pressures. Of significance for large scale production is the synthesis of ethanol from ethane and of isopropanol from propene. The production of these alcohols takes place in the presence of acidic catalysts, wherein usually a catalyst carrier consisting of an alumosilicate and a silicate material is used, which has been impregnated with phosphoric acid.

The material of the catalyst carrier is usually built up of pure silicic acid like for example silica gel (US Patent No. 2,579,601) or consists of silicic acid with a varying amount of alumina (US Patent No. 3,311,568) and consists of pure lattice-layer silicates (sheet-structure silicates), for example those containing montmorillonite (DE 29 08 491), respectively.

Apart from these phosphoric acid-containing catalyst carriers, also zeolithic materials are used (EP 0 323 269 B1) or other acidic catalysts like for example zircon phosphate (GB 00 55 34).

Until now for carriers which are based on silicic acid in the form of silica gel exclusively, the mechanical hardness is questionable over a longer hold up time. Aluminium containing catalyst carriers or those consisting of only alumina show a noticeably higher long-term stability, but they have the immense disadvantage that aluminium is leached out from the catalyst carrier during the hydration reaction due to the effect of phosphoric acid. The aluminium ends up in the succeeding apparatuses as poorly soluble sedimentations in the form of aluminium phosphate. As a result over time the downstream apparatus becomes blocked.

In DE 1 156 772 a process is described for reducing the aluminium content of the lattice-layer silicate by reaction with hydrochloric acid. However, even after intensive washing with hydrochloric acid the carrier material still shows the presence of approximately 1 to 2% by weight of aluminium.

In EP 0 578 441 B1 by using a pelletised silicate carrier based on aerosil (Degussa) which does not contain aluminium a certain long-term stability is achieved. The starting material for the production of aerosil is the relatively expensive silicon tetrachloride. Since materials based on lattice-layer silicates, such as montmorillonite for example, are natural raw materials which can be excavated from relevant deposits in the earth, these have an obvious economic advantage over pelletised silicate carriers.

Clearly it would be advantageous if a process could be devised for the hydration of C_2 and C_3 olefins with water in the presence of a catalyst which comprises a catalyst carrier impregnated with acid having a high long term stability and which leached out reduced amounts of aluminium during the hydration reaction.

Applicant has surprisingly and unexpectedly found that a dealuminated catalyst carrier based mainly on aluminium-containing lattice-layer silicates with a montmorillonite structure, and an aluminium content of less than 0.3% by weight has a long-term stability.

According to one aspect of this invention there is provided a catalyst/catalyst carrier with an aluminium content of less than 0.3 % by weight obtainable from mainly layer-lattice silicates which contain aluminium by a dealuminating process.

According to another aspect of the present invention there is provided a process for the reduction of the aluminium content of a catalyst carrier which comprises mainly aluminium-containing lattice-layer silicates with a montmorillonite structure, wherein the catalytic carrier is

- impregnated with phosphoric acid
- treated hydrothermally at a temperature of between 160 and 300°C and a partial water vapour pressure or 4 to 80 $\text{bar}_{\text{absolute}}$

- washed subsequently with an acidic, basic or neutral solution at a temperature of between 20 and 100 °C, and
- afterwards rinsed with water until the washing water becomes neutral.

According to yet another aspect of the present invention there is provided a process for the hydration of C_2 or C_3 olefins with water in the presence of a catalyst that comprises a catalyst carrier impregnated with acid as described above with reference to the previous aspects of the invention.

During a process of hydrating C_2 or C_3 olefins with water in the presence of a catalyst as described above in the first aspect of the invention only very small amounts of aluminium are washed out of the catalyst carrier.

The terms hydration and hydration reaction refer, for the purpose of this invention, to the reaction of water with a carbon-carbon double bond.

The terms dealuminating and dealuminated catalyst carrier, respectively refer for the purposes of this invention, to the process of reducing the aluminium content and a catalytic carrier with a reduced aluminium content.

By carrying out the process according to the invention a catalyst carrier can be produced which is based on calcined and subsequently treated lattice-layer silicates, that has a noticeably reduced aluminium content compared to a catalyst carrier which has not been treated according to this invention. In spite of the reduced aluminium content, the long-term stability of the catalyst has been maintained. By using a catalyst carrier according to this invention during the process also according to this invention for the hydration of C_2 or C_3 olefins with water, the amount of aluminium leaching out during the hydration reaction is noticeably reduced. Thus fewer insoluble aluminium compounds are produced during the hydration reaction, which in conventional processes lower the hold up time of the succeeding apparatuses, such as heat exchangers, by blocking the pipes or the areas of heat exchange.

The dealuminized catalytic carrier according to this invention with an aluminium content of less than 0.3 % by weight contains mostly aluminium-containing lattice-layer silicates. In particularly preferred forms the dealuminized catalytic carrier according to this invention has an aluminium content of less than 0.03 % by weight. The aluminium-containing lattice-layer silicates are preferably smectites and have preferably montmorillonite structures. Lattice-layer silicates with montmorillonite structures are for example the bentonites. Apart from the montmorillonites, bentonites can obtain other components for example mica, illite, crystobalite and zeolite.

The starting materials for the production of a catalyst carrier according to the invention are conventional catalyst carriers, for example based on calcined and subsequently treated lattice-layer silicates.

The dealuminized catalyst carrier according to this invention with an aluminium content of less than 0.3 % by weight, preferably less than 0.03 % by weight, based on mainly aluminium rich lattice-layer silicates with a montmorillonite structure can be made by impregnating the catalyst carrier with phosphoric acid preferably a 10 to 90 % by weight phosphoric acid, in particular preferred a phosphoric acid of 50 to 60 % by weight so that the catalyst carrier contains between 5 and 60 %, preferably between 30 and 40 % phosphoric acid, followed by hydrothermal treatment at a temperature of between 160 and 300 °C, preferably at a temperature of between 220 and 260 °C and a partial water vapour pressure of between 4 and 80 bar$_{\text{absolute}}$, preferably at a partial water vapour pressure of between 16 and 25 bar$_{\text{absolute}}$, followed by washing with an acidic, basic or neutral solution, preferably an acidic or neutral solution, in particular with water, hydrochloric acid or water containing 0 to 30 parts concentrated hydrochloric acid at a temperature of between 20 and 100 °C, preferably of between 70 and 90 °C and afterwards rinsing the catalyst carrier until the washing water has become neutral.

A example of how to carry out the process according to the invention for reducing the aluminium content of a catalyst carrier is described below, without limiting the process of the present invention to this example.

For the reduction of the aluminium content of a catalyst carrier which comprises mostly aluminium-containing lattice-layer silicates commercial lattice-layer silicates such as, for example, montmorillonite or bentonite containing catalyst carriers can be used. The catalyst carriers have preferably the form of spherical shapes, such as for example balls, lenses, cuboids, cylinders or also irregular forms, in particular preferred they have the shape of balls. The spherical shapes have preferably an average diameter of 1 to 10 mm, most preferred a diameter of 4 to 6 mm.

For the reduction of the aluminium content in the catalyst carrier it is impregnated with acid, treated hydrothermally, subsequently washed and afterwards rinsed.

The catalyst carrier is impregnated with acid, preferably phosphoric acid in order to produce the effect according to the invention. A 10 to 90 % by weight phosphoric acid, preferably a 50 to 60 % by weight phosphoric acid is used. After being impregnated, the catalyst carrier should show an amount of phosphoric acid of 5 to 60 % by weight, preferably 30 to 40 % by weight. Afterwards the catalyst carrier is treated hydrothermally.

Under the hydrothermal conditions the lattice-layer silicate material, like for example montmorillonite changes into cristobalite-like structures. Accompanying the micropores, that were previously present, disappear. This morphological changes in structure can clearly be seen by the BET surface, the pore volume and the distribution of pore radii. Under hydrothermal reaction conditions the so-called "open" pore structures are attained.

Hydrothermal treatment of the catalyst carrier containing lattice-layer silicates can be carried out at temperatures of between 160 and 300 °C under a partial water vapour pressure of between 4 and 80 $\text{bar}_{\text{absolute}}$, preferably between 220 and 260 °C and a partial water vapour pressure of between 16 and 25 $\text{bar}_{\text{absolute}}$.

After hydrothermal treatment the catalyst carrier is washed with a basic, acidic or neutral solution, preferably with an acidic or neutral solution and in particular preferred with hydrochloric acid, with water containing 0 to 30 parts concentrated hydrochloric acid or with a neutral aqueous solution. The washing of the catalyst carrier is carried out at a temperature of between 20 and 100 °C, preferably between 70 and 90 °C.

After said washing the catalyst carrier can be rinsed with water until the washing water used to rinse becomes neutral.

The catalyst carrier then has a cumulated pore volume of between 0.2 and 0.9 ml/g, preferably between 0.6 and 0.7 ml/g. The compressive strength of the catalyst carrier should be at least 10 N/mm, preferably at least 20 N/mm.

In a specific embodiment of the process according to the invention, the hydrothermal treatment of the catalyst carrier impregnated with acid, which contains 5 to 60 % by weight phosphoric acid, preferably 30 to 40 % by weight takes place by use as a catalyst in a hydration reaction by C_2 or C_3 olefins. For impregnating the catalytic carrier preferably a 10 to 90 % by weight phosphoric acid, most preferably a 30 to 60 % by weight phosphoric acid is used.

During this hydration in a reactor filled with catalyst, preferably a tubular reactor, olefin and water in a molar ratio of between 0.1 and 0.8, preferably between 0.15 and 0.5 are reacted. The olefin to be used and the water to be used are introduced into the reactor in gaseous or liquid form, preferably gaseous. For evaporating the water and heating both reagents to reaction temperature, respectfully it may be beneficial to introduce both reagents into the reactor over a vaporisation or thermostat-controlled section, which is heated to the reaction temperature electrically or by way of heat carriers which leads into the reactor. The gas hourly space velocity (GHSV) should be between 10 and 100 $l_n/min/l_{cat}$. The hydration reaction is be carried out at a temperature of between 160 and 300 °C and an absolute pressure of between 20 and 200 bar. The hydration of ethene to ethanol is carried out preferably at a temperature of between 220 and 260 °C and an absolute pressure of between 60 and 80 bar.

The exit of the reactor can preferably be connected to a cooler which condenses out the majority of the sub-critical components and makes them accessible to further reprocessing for example by fractionation or distillation.

For controlling the activity and selectivity of the catalyst carrier impregnated with acid it can be advantageous to analyse the the outflow of the reactor. The analysis can be carried out by gas chromatography.

To increase the lifetime of the catalyst is it advantageous to add the acid, with which the catalyst carrier has been impregnated, into the reactor continuously or discontinuously preferably continuously. The acid can be introduced into the reactor for example by injection. The amount of acid which is introduced into the reactor can be made dependent on the results of the analysis of the outflow. The resulting amount of acid to be introduced can be calculated from the analysis of the outlet stream.

After the hydrothermal treatment of the catalyst carrier being used as a catalyst in a hydration reaction, the remaining acid with which the catalyst carrier has been impregnated is removed by washing with water until the washing water becomes neutral.

After the removal of the remaining acid the catalyst carrier is washed with a basic, acidic or neutral solution, preferably with an acidic or neutral solution and in particular preferably with hydrochloric acid, with water which contains 0 to 30 parts concentrated hydrochloric acid or a neutral aqueous solution. The catalyst carrier can be washed at a temperature of between 20 and 100 °C, preferably at a temperature of between 70 and 90 °C.

After the washing the catalyst carrier can be rinsed with water until the washing water becomes neutral.

In the case of catalyst carriers which by being used as catalysts in a hydration reaction have been hydrothermally treated, it may be advantageous, after reducing the aluminium content in the catalyst carrier, to clean off the catalyst carrier by burning off possible attached carbon compounds, eg at a temperature of between 300 and 1,000 ^{0}C, preferably between 450 and 500 ^{0}C.

Both variations of the process according to this invention result in a treated catalyst carrier with a reduced aluminium content. The treated catalyst carriers have an average diameter of between 1 and 10 mm, preferably however of between 4 and 6 mm. The total pore volume is between 0.2 and 0.9 ml/g, preferably between 0.6 and 0.7 ml/g. The compressive strength after the treatment of the catalyst carrier is at least 10 N/mm, preferably 20 N/mm. The amount of aluminium in the treated catalyst carriers is less than 0.3 % by weight, preferably less than 0.03 % by weight.

The catalyst carriers produced by the process according to this invention with reduced aluminium content can be used for the production of catalysts.

The catalyst carriers produced by the process according to this invention with a reduced aluminium content can according to the invention be used for the hydration of C_2 or C_3 olefins with water in the presence of a catalyst, which consists mainly of a catalyst carrier treated according to the invention having been impregnated with acid.

Preferably the catalyst carrier is impregnated with an acid, preferably phosphoric acid. The quantity of phosphoric acid should be between 5 and 60 % by weight, preferably between 30 and 40% by weight to obtain the maximum catalytic activity of the impregnated catalyst carrier. For impregnating the catalyst carrier an aqueous phosphoric acid solution which contains a phosphoric acid quantity of between 10 to 90 % by weight, preferably between 50 and 60 % by weight is used. The acidic catalyst thus produced is filled in a reactor, preferably a tubular reactor. The reactor is operated isothermally or non-isothermally, preferably isothermally and can be heated electronically or by way of heat carriers.

The reactor is fed continuously or discontinuously, preferably continuously, with the reagents water and C_2 or C_3 olefin. The ratio of water to olefin with which the reagents are fed into the reactor is adjusted at a molar ratio of between 0.1 to 0.8, preferably between 0.15 and 0.5 . The molar ratio can be adjusted by using for example a mass flowmeter. Both reagents can be introduced into the reactor liquid or gaseous, preferably gaseous. For evaporating the water and heating both reagents to reaction temperature respectively it may be beneficial to introduce both reagents into the reactor over a vaporisation or thermostat-controlled section, which is heated to the reaction temperature electrically or by way of heat carriers. The temperature in the reactor and the temperature with which the reagents flow into the reactor should be between 160 and 300 °C.

For the hydration reaction of ethene to ethanol, the temperature in the reactor and the temperature with which the reagents flow into the reactor is preferably between 220 and 260 °C. The pressure in the reactor is in the range of between 20 and 200 bar$_{\text{absolute}}$, preferably between 60 and 80 bar$_{\text{absolute}}$.

The exit of the reactor is preferably connected to a cooler, which can condense out the majority of the components and make these accessible to further reprocessing.

To control the activity and selectivity of the acid impregnated catalyst carrier, it can be beneficial to analyse the outflow of the reactor. This analysis can be carried out by for example gas chromatography.

To increase the lifetime of the catalyst it is advantageous to add the acid, preferably phosphoric acid, with which the catalyst carrier has been impregnated, into the reactor continuously or discontinuously, preferably continuously. The acid can be introduced into the reactor for example by injection. The amount of acid which is introduced into the reactor can be made dependent on the results of the analysis of the outflow. Both the analysis of the outflow and the determination resulting amount of acid to be introduced can be carried out by automation.

Figure 1 and Figure 2 show the rate of consumption of ethene and the rate of formation of ethanol in dependence of the reaction time by using differently treated catalyst carriers without limiting the process according to this invention to these results.

Figure 1

In figure 1 the rate of consumption of ethene during a hydration reaction is shown in dependence of the reaction time. The data from four experiments are shown. The measurements represented by circles refer to the rate of consumption of ethene relative to reaction time when a new catalyst carrier containing the original amount of aluminium is used. The data of the rate of consumption of ethene represented by squares result from three series of experiments which were carried out using a catalyst carrier with a reduced aluminium content.

Figure 2

In figure 2 the rate of formation of ethanol during in a hydration reaction in dependence of the reaction time is shown. The data from four experiments are shown. The measurements represented by circles refer to the rate of formation of ethanol relative to reaction time when a new catalyst carrier containing the original amount of aluminium is used. The data of the rate of formation of ethanol represented by squares refer result from three series of experiments which were carried out using a catalyst carrier with a reduced aluminium content.

The process according to the present invention is described by the examples below without being limited to these examples.

Example 1: The synthesis of ethanol with an untreated catalyst carrier

The experiment took place in a pilot plant whose core part contains an isothermally operated tubular reactor of 1,000 mm in length and 48 mm diameter.

The reagents water and ethene are introduced into the reactor over a vaporisation or thermostat-controlled section, which is electrically heated to the reaction temperature. The water is introduced liquidly through a pump, while ethene is taken from a 130 bar steel flask. The introduction of a mixture of ethene : water at a molar ratio of 0.3 : 1 is controlled by a mass flowmeter.

The exit of the reactor is connected to a cooler which condenses out the majority of the subcritical components, mainly ethanol, water and diethylether, the rest is diverted to the waste gas whose volumetric flow is measured by a gas-meter. A part of the waste gas is fed through a bypass into a gas chromatograph. The liquid products are also analysed by gas chromatography.

The synthesis of ethanol according to the present example was measured at a temperature of 240 °C and a pressure of 70 $\text{bar}_{\text{absolute}}$. The standard test conditions are summarised in Table 1. The catalyst used was an untreated new catalyst carrier, the KA-1 of Südchemie AG. The properties of the carrier are summarised in Table 2. Conversion and selectivity values reached at the start of the experiment are included in Table 2.

To determine the aluminium content of the catalyst carrier this was analysed with an atomic emission spectrometer before the start of an experiment. The atomic emission spectrometer used was an inductively coupled plasma atomic emission spectrometer (ICP-AES) JY 38+ made by ISA Jobin Y. The results of the analysis are shown in Table 2.

Example 2: The synthesis of ethanol with an untreated old carrier

The experiment was repeated in the same way as described in Example 1. This time an untreated catalyst carrier that had already been used for the catalysis of a hydration reaction is employed ('old carrier'). Again the standard test conditions shown in Table 1 are relevant. The results of the experiment as well as the properties of the catalyst carrier are given in Table 2.

As can be seen from the values in Table 2, the specific surface of the impregnated catalyst carrier decreases after the catalyst has been used only once. Similarly the aluminium content is reduced to approximately ¼ of its original value by the single use as catalyst. The remaining ¾ of the original amount of aluminium in the untreated new carrier are leached out during the hydration reaction. This aluminium forms the insoluble sedimentations which hinders the reprocessing steps.

Example 3: The synthesis of ethanol with a treated old carrier

The experiment was carried out in the same way as described in Example 1. As catalyst carrier an already used old carrier was employed whose aluminium content had been reduced by treatment according to the process of this invention. Again the standard test conditions shown in Table 1 are relevant. The results of the experiment as well as the properties of the catalyst carrier are also given in Table 2.

The deactivation of the catalyst carrier with, as well as without, a reduced aluminium content are represented in both Figure 1 and Figure 2.

As can be seen from Table 2 the aluminium content of a catalyst carrier is reduced to less than 0.03 % by weight by treating the old carrier in the process according to this invention. This value represents the detection limit of the atomic emission spectrometer used. The compressive strength of the treated old carrier is 30 N/mm sufficient to guarantee good long-term stability of the catalyst carrier.

In spite of treating the catalyst carrier and reducing its aluminium content to a value less than 0.03 % by weight, the conversion of ethylene and the yield of ethanol both remained good compared to an untreated, unused catalyst carrier ('new carrier') and to an untreated old carrier, respectively, even slightly increased in the present example.

As can be seen from Figure 1 and Figure 2 reducing the aluminium content according to the process of the invention has no influence on the rate of consumption of ethene nor on the rate of formation of ethanol.

Standard experimental conditions	
Process Parameter	*Value*
total reaction pressure	70 bar
temperature of the reactor (isotherm)	240°C
GHSV	21.3 l_n/min/l_{cat}
water : ethene	1.0 : 0.3 mol : mol
carrier material	KA-1 (Südchemie)

Table 1: The standard experimental conditions used in all experiments.

Property (impregnated carrier)	*New Carrier*	*Untreated Old Carrier*	*Treated Old Carrier*
force withstood	20 N/mm	40 N/mm	30 N/mm
spec. surface (BET)	20 m^2/g	4 m^2/g	3 m^2/g
cumulated pore volume	0.7 ml/g	0.4 ml/g	0.4 ml/g
Al content	1.3 % b.w.	0.31 % b.w.	< 0.03 % b.w.
Si content	25 % b.w.	25 % b.w.	24 % b.w.
H_2PO_4 content	35 % b.w.	36 % b.w.	35 % b.w.
ethene turnover at start of experiment	5 %	5 %	6 %
volume-time yield (ethanol) at start of experiment	77.4 $g/l_{cat}/hr$	76.4 $g/l_{cat}/hr$	79.8 $g/l_{cat}/hr$

Table 2: A comparison of the properties of the three types of catalyst carriers used

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A catalyst/catalyst carrier with an aluminium content of less than 0.3 % by weight obtainable from mainly layer-lattice silicates which contain aluminium by a dealuminating process.

2. A catalyst/catalyst carrier according to claim 1, wherein said catalyst/catalyst carrier has an aluminium content of less than 0.03 % by weight.

3. A catalyst/catalyst carrier according to any one of the preceding claims, wherein said layer-lattice silicates used are smectite.

4. A catalyst/catalyst carrier according to any one of claims 1 to 3, wherein said layer-lattice silicates have montmorillonite structures.

5. A catalyst/catalyst carrier according to any one of the preceding claims, wherein said catalyst carrier has a cumulative pore volume of between 0.2 and 0.9 ml/g.

6. A catalyst/catalyst carrier according to any one of the preceding claims, wherein said catalyst/catalyst carrier has a total pore volume of between 0.6 and 0.7 ml/g.

7. A catalyst/catalyst carrier according to any one of the preceding claims, wherein said catalyst/catalyst carrier has the shape of a spherical body or ball.

8. A catalyst/catalyst carrier according to any one of the preceding claims, wherein said catalyst/catalyst carrier has a diameter of between 1 and 10 mm.

9. A catalyst/catalyst carrier according to any one of the preceding claims, wherein said catalyst/catalyst carrier has a diameter of between 4 and 6 mm.

10. A catalyst/catalyst carrier according to any one of the preceding claims, wherein said catalyst/catalyst carrier has a compressive strength of at least 10 N/mm.

11. A catalyst/catalyst carrier according to any one of the preceding claims, wherein said catalyst/catalyst carrier has a compressive strength of at least 20 N/mm.

12. A catalyst/catalyst carrier according to any one of the preceding claims, wherein said catalyst/catalyst carrier is obtainable from the lattice-layer silicates containing aluminium by carrying out the following steps:

- impregnating with an acid,
- treating hydrothermally, and
- washing with an acidic, a basic or a neutral solution.

13. A catalyst/catalyst carrier according to claim 12, wherein said step

- of impregnating with an acid comprises impregnating with a mineral acid which is phosphoric acid, and which includes the further step of rinsing with water.

14. A catalyst/catalyst carrier according to claim 12 or claim 13, wherein said step

- of hydrothermal treatment takes place at a temparure of between 160 and 300^{0}C and/or at a partial water vapour pressure of between 4 and 80 bar$_{abs}$.

15. A catalyst/catalyst carrier according to any one of claims 12 to 14, wherein said step

- of hydrothermal treatment takes place at a temperature of between 220 and 260^0 C and/or at a partial water vapour pressure of between 16 and 25 bar$_{abs}$.

16. A catalyst/catalyst carrier according to any one of the claims 12 to 15, wherein said step

- of hydrothermal treatment takes place completely or in part during the use of said catalyst/catalyst carrier in a hydration reaction.

17. A catalyst/catalyst carrier according to any one of claims 12 to 16, wherein said step

- of washing takes place at a temperature of between 20 and 100^0 C.

18. A catalyst/catalyst carrier according to any one of claims 12 to 17, wherein said step

- of washing takes place at a temperature of between 70 and 90^0 C.

19. A catalyst/catalyst carrier according to any one of claims 12 to 18, wherein said step of washing takes place with water, with hydrochloric acid, or with water containing 0 to 30 parts of concentrated hydrochloric acid.

20. A catalyst/catalyst carrier according to claim 13, wherein said step of rinsing takes place until the washing water becomes neutral.

21. A process for producing a catalyst/catalyst carrier according to any one of claims 1 to 11, by a process of treating lattice-layer silicates which includes the following steps
impregnating with an acid,
- treating hydrothermally, and
- washing with an acidic, a basic or a neutral solution.

22. A process according to claim 21, wherein the catalyst/catalyst carrier is purified by burning off adhering organic carbon-containing compounds at a temperature of between 300 and 1,000^0 C before the steps defined in claim 21 are carried out and further including the steps claimed in claims 13 to 19.

23. A process for the hydration of olefins, preferably C_2 or C_3 olefins, comprising hydrating the olefins with water in the presence of at least one catalyst, which is made from a catalyst/catalyst carrier according to any one of claims 1 to 20 impregnated with acid.

24. A process according to claim 23, wherein the hydration reaction
- is carried out in a reactor
- an olefin to water molar ratio is adjusted to between 0.1 and 0.8 in the reactor
- has a gas hourly space velocity of 10 to 100 l_n/min/l_{cat}.
- said catalyst contains 5 to 60 % by weight of acid, and
- the hydration reaction of the olefins is carried out at a temperature of between 160 and 300^0 C and a pressure of between 20 and 200 $\text{bar}_{\text{absolute}}$.

25. A process according to claim 23 or claim 24, wherein said acid with which the catalyst/catalyst carrier is impregnated comprises 10 to 90 % by weight phosphoric acid.

26. A process according to claim 25, wherein said acid with which the catalyst/catalyst carrier is impregnated comprises 50 to 60 % by weight phosphoric acid.

27. A process according to any one of claims 23 to 26, wherein said catalyst contains 5 to 60 % of an acid, calculated as pure acid and the acid is a mineral acid.

28. A process according to any one of claims 23 to 27, wherein the hydration reaction for producing ethanol from ethene is carried out at a temperature of between 220 and 260^0 C and a pressure of between 60 and 80 bar.

29. A process according to any one of claims 23 to 28, wherein the olefin used and the water used are introduced into the reactor in gaseous form.

30. A process according to any one of claims 23 to 29, wherein said acid is introduced into the reactor during the course of the hydration reaction.

31. A process according to claim 30, wherein said acid used is phosphoric acid.

32. A process according to any one of claims 23 to 31, wherein said acid is injected into the reactor continuously.

33. A catalyst for the hydration of olefins to alcohols obtainable by bringing into contact the catalyst/catalyst carrier according to any one of claims 1 to 20 and a mineral acid.

34. A catalyst according to claim 33, wherein the mineral acid is phosphoric acid.

35. A catalyst for the hydration of olefins to alcohols according to claim 33, which contains 5 to 60 % by weight acid, calculated as pure acid.

36. A catalyst/catalyst carrier according to any one of the claims 1 to 20, wherein the said catalyst/catalyst carrier has at least partly a cristobalite-like structure.

37. A catalyst/catalyst carrier with an aluminium content of less than 0.3 % by weight substantially as herein described with reference to any one of the examples.

38. A process for producing a catalyst/catalyst carrier substantially as herein described with reference to any one of the examples.

39. A catalyst for the hydration of olefins to alcohols substantially as herein described with reference to any one of the examples.

DATED THIS SEVENTEENTH DAY OF APRIL 2001.

RWE-DEA AKTIENGESELLSCHAFT FÜR MINERALOEL UND CHEMIE

BY

PIZZEYS PATENT AND TRADE MARK ATTORNEYS

Figure 1:

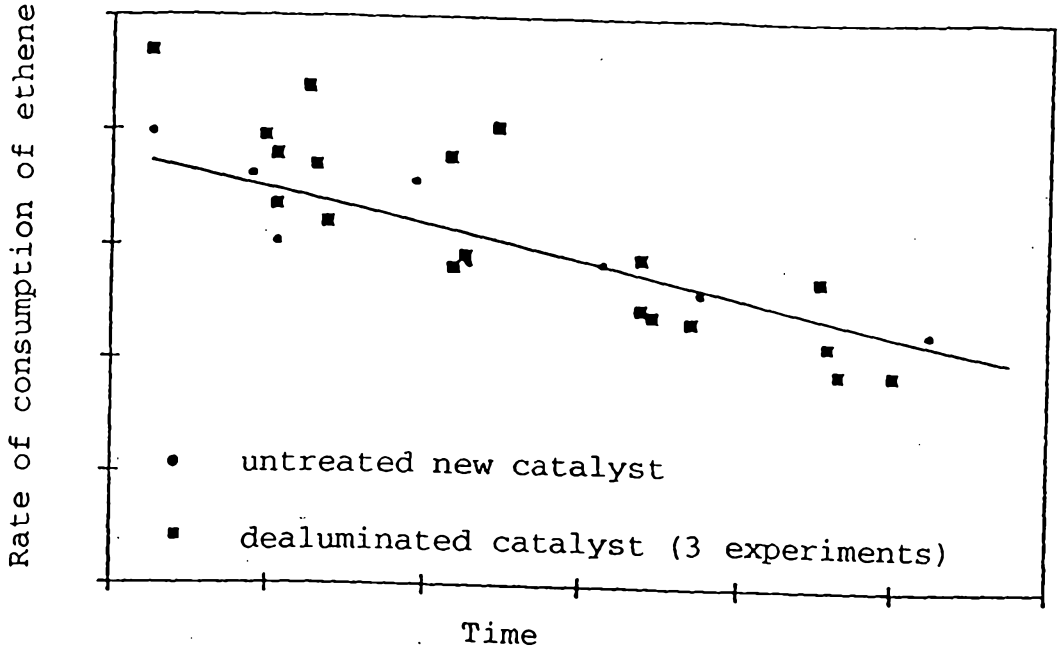

Figure 2: