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(54) HYDROTHERMAL TREATMENT OF SILICA IN THE PRESENCE OF A
 TI-COMPOUND

- (71) We, SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V., a company organised under the laws of The Netherlands, of 30 Carel van Bylandtlaan, the Hague, The Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-
- The invention relates to a process for suppressing the increase in specific average pore diameter which occurs when a silica is subjected to a hydrothermal treatment.
- Porous silica is used widely, inter alia, as a drying agent, a catalyst, a catalyst carrier and as an adsorbent in chromatographic separations. In each of these applications the specific average pore diameter of the silica plays a more or less important part. In this patent application the specific average pore diameter will, for the sake or brevity, be indicated by the letter p. For further information about p and the way in which it is determined reference is made to Netherlands patent application No. 7214397, in which this catalyst characteristic is discussed in detail.
- It is very important that once a silica has the proper p for a certain application, this p should change as little as possible during all further treatments to which the silica is subjected. However, sometimes the problem arises that p of a silica increases when it is subjected to a hydrothermal treatment, by which is understood that the silica is treated at elevated temperature with liquid water and/or water vapour.
- For reasons hitherto unknown, with a number of silicas the hydrothermal treatment has little or no effect on p. It has further been found that under certain conditions of temperature and pressure a hydrothermal treatment may cause a much stronger increase in p with one silica than with another. It should be mentioned here that, in general, when a silica shows a distinct increase in p upon hydrothermal treatment, this increase is larger as the treatment is effected under more severe conditions, i.e. at a higher temperature and/or pressure.
- Since especially in the application of catalysts, in particular to hydrocarbon treating processes such as hydrosulphurization and demetallization of residual oils, as well as in the regeneration of such catalysts, the Applicant was, in the past, regularly confronted with the above-mentioned problems concerning the increase in p of silicas under hydrothermal conditions, it was decided to carry out an extensive investigation to provide more insight into this matter. In this investigation it was found that the increase in p, which occurs when silicas are subjected to a hydrothermal treatment, can be greatly suppressed by carrying out this treatment in the presence of an added quantity of a Ti-compound.
- This finding is thought to be very important, because it greatly enhances the applicability of silicas and in principle enables silicas to be exposed to hydrothermal conditions without the risk of too great an increase in p. This finding is the subject of the present patent application.
- The present application therefore relates to a process for suppressing the increase in p which occurs when a silica is subjected to a hydrothermal treatment, the treatment being carried out in the presence of an added quantity of a Ti-compound.
- In the process according to the invention the silica comes into contact at elevated temperature with liquid water and/or water vapour. This contact may occur at atmospheric pressure as well as at elevated pressure.
- When in the process according to the invention the silica comes into contact with liquid water, and also when it comes into contact with water vapour, the addition of a compound of Ti may occur by emplacing this compound on the silica before it comes into contact with the

liquid water or the water vapour. The emplacement of the compound concerned on the silica may very suitably be effected by impregnating the silica with one or more solutions of the compound concerned followed by drying and, if desired, calcination. When the silica comes into contact with liquid water at elevated temperature, the addition of the compound concerned may also very suitably be carried out by adding a water-soluble compound to this water.

In the embodiments of the process according to the invention described so far the compound concerned is added either to the silica prior to the hydrothermal treatment, or to the liquid water used in the hydrothermal treatment. The process according to the invention may also be carried out successfully using a combination of the two ways of addition. To this end the compound concerned is first emplaced on the silica, after which it is treated, at an elevated temperature, with liquid water to which the compound concerned has been added.

The quantity of the compound concerned to be added in the process according to the invention is substantially determined by the five following factors:

- 1) The increase in p deemed permissible;
- 2) The temperature used in the treatment;
- 3) The pressure used in the treatment;
- 4) The quantities of Mg, Al and Ti present in the silica to be treated;
- 5) The quantities of K, Na and Ca present in the silica to be treated.

It may be stated that in general the influence of each of these factors, when the other four remain constant, is such that the quantity of the compound concerned to be added in the process according to the invention is larger according as

- 1) a stronger suppression of the increase in p is envisaged;
- 2) a higher temperature is used in the treatment;
- 3) a higher pressure is used in the treatment;
- 4) the quantities of Mg, Al and Ti present in the silica to be treated are smaller, and
- 5) the quantities of K, Na and Ca present in the silica to be treated are larger.

When the impregnation route is used, the quantities of the compounds concerned which in the most common cases have to be incorporated into the silica to achieve the effect envisaged, are as a rule such that the silica to be treated contains more than 0.1 g and not more than 5 g of the active element per 100 g.

The quantity of the compound concerned to be used to realize a certain degree of suppression of the increase in p can, under specific conditions of the hydrothermal treatment, be determined with the aid of some simple experiments.

The process according to the invention is in general important for suppressing the increase in p which occurs when silicas are exposed to hydrothermal conditions. The process is important especially in the use of silicas as catalysts and catalyst carriers, in particular for hydrocarbon treating processes such as hydrodesulphurization and demetallization of residual oils and in the regeneration of such catalysts.

The present patent application is based on results of a thorough investigation, carried out by the Applicant, into the influence of hydrothermal conditions on p of silicas. The p of a silica can be increased by subjecting this silica to a hydrothermal treatment in the presence of an added quantity of one or more compounds selected from the group formed by compounds of the elements Li, K, Na, Cs, Rb, Ca, Sr and Ba as well as NH_4 -compounds and NH_3 .

Continued investigation has led to the following interesting process combination.

Suppose that a silica is available which, as regards such properties as particle size, total pore volume and mechanical strength, is considered very suitable for a certain application, but that this silica has too small a p to be eligible for this application. A silica having the proper p can be prepared from this silica in a simple way by subjecting it to a hydrothermal treatment in the presence of an added quantity of one or more of the compounds mentioned above. As a result of this treatment the susceptibility of the silica for hydrothermal conditions has greatly increased. When the silica is subsequently used for an application in which it is exposed to hydrothermal conditions, there is a great risk of the p of the silica exceeding the permissible value. By applying the process according to the present patent application to a silica whose p has been increased above this problem is obviated and a silica is obtained whose p is considerably less sensitive to hydrothermal conditions.

The above-described process combination can very suitably be used in the hydrodemetallization of residual oils using a catalyst consisting substantially of silica in cases where the available silica has too small a p and where it is, moreover, intended in the regeneration of the deactivated catalyst to use a hydrothermal treatment such as a steam treatment.

The invention will now be explained with reference to the following example.

Example

Two different hydrothermal treatments (1-2) were applied to silica I and to three silicas ID, IE and IF which had been prepared from silica I as the starting material. Silica I had an Al-content of 0.1 %w, a total pore volume of 0.9 ml/g a crushing strength higher than 16.7

kg/cm², and it was available in the form of spheres with a diameter of 1-3mm. Silica I had a p of 10 nm and a Na-content of 0.1 %w. The preparation of silicas ID, IE and IF was effected by impregnating three portions of silica I with a solution of $Ti(OC_3H_7)_4$ in a mixture of isopropyl alcohol and acetylacetone followed by drying at 120°C and two hours calcination at 400°C.

5 The silicas ID, IE and IF thus obtained had Ti-contents of 1, 2.5 and 5 %w, respectively. 5

The various hydrothermal treatments were carried out as follows.

Treatment 1

A mixture of 15 ml silica and 19 ml water was heated in an autoclave under autogenous pressure to 230°C and then maintained at this temperature for two hours.

10 Treatment 2

A mixture of 15 ml silica and 19 ml of an aqueous 2×10^{-3} molar Na_2CO_3 solution was heated in an autoclave under autogenous pressure to 230°C and then maintained at this temperature for two hours.

15 The results of the experiments are given in the following table. For the determination of p of the silicas use was made of the nitrogen adsorption/desorption method and of the mercury penetration method, as described in Netherlands patent application No. 7214397. 15

Table

20	Exp. No.	Silica No.	Hydrothermal treatment No.	p of the silica after hydrothermal treatment, nm	20
	A	I	1	18	
25	B	I	2	65	25
	1	ID	2	36	
	2	IE	2	24	
	3	IF	2	21	
30					30

Of the experiments listed only Nos. 1-3 are experiments according to the invention. Experiments A and B are outside the scope of the invention and have been included in the patent application for comparison.

35 The results presented in the table give rise to the following remarks. 35

1) Comparison of experiments A and B shows that the effect of a hydrothermal treatment with liquid water on p of a silica is greater when a Na-compound is dissolved in the water.

2) Comparison of experiments B, 1, 2 and 3, with each other shows that the effect on p of a silica of a hydrothermal treatment carried out with liquid water in which a Na-compound has been dissolved is strongly suppressed when the Ti-content of the silica has previously been increased by impregnation with a compound of this element.

WHAT WE CLAIM IS:-

1. A process for suppressing the increase in specific average pore diameter which occurs when a silica is subjected to a hydrothermal treatment, characterized in that the hydrothermal treatment is carried out in the presence of an added quantity of a Ti-compound.

2. A process according to claim 1, characterized in that the compound concerned is emplaced on the silica before it is subjected to the hydrothermal treatment.

3. A process according to claim 2, characterized in that the emplacement of the compound concerned is effected by impregnating the silica with one or more solutions of the compound concerned followed by drying and, if desired calcination.

4. A process according to claim 1, characterized in that the compound concerned is added in the form of a water-soluble compound to the liquid water that is used for the hydrothermal treatment.

5. A process according to any one of claims 1-4, characterized in that the compound concerned is emplaced on the silica before it is subjected to the hydrothermal treatment and that the hydrothermal treatment is carried out by treating the silica at elevated temperature with liquid water to which the compound concerned has been added.

6. A process according to any one of claims 1-5, characterized in that it is applied to a silica whose specific average pore diameter has been increased by subjecting it to a hydrothermal treatment in the presence of an added quantity of one or more compounds selected from the group formed by compounds of the elements Li, K, Nb, Rb, Cs, Ca, Sr, Ba as well as NH_4 -compounds and NH_3 .

7. A process for suppressing the increase in specific average pore diameter which occurs when a silica is subjected to a hydrothermal treatment, substantially as described hereinbefore and in particular with reference to experiments 1-3 of the example.

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