

12

**EUROPEAN PATENT APPLICATION**

21 Application number: **88202328.6**

51 Int. Cl.4: **B01J 37/00 , B01J 32/00 ,**  
**B01J 21/12**

22 Date of filing: **18.10.88**

30 Priority: **19.10.87 GB 8724436**

43 Date of publication of application:  
**26.04.89 Bulletin 89/17**

64 Designated Contracting States:  
**AT BE DE ES FR GB IT LU NL SE**

71 Applicant: **SHELL INTERNATIONALE**  
**RESEARCH MAATSCHAPPIJ B.V.**  
**Carel van Bylandtlaan 30**  
**NL-2596 HR Den Haag(NL)**

72 Inventor: **Daamen, Jacobus Theodorus**  
**Badhuisweg 3**  
**NL-1031 CM Amsterdam(NL)**  
Inventor: **Huizinga, Tom**  
**Badhuisweg 3**  
**NL-1031 CM Amsterdam(NL)**

74 Representative: **Aalbers, Onno et al**  
**P.O. Box 302**  
**NL-2501 CH The Hague(NL)**

54 **Silica-alumina extrudates.**

57 The invention relates to a process for the preparation of a shapable dough which comprises mixing and kneading a particulate silica-alumina with water and with an alkanolamine or ammonia to obtain a mixture having, a total solids content of from 25 to 60% by weight, the alkanolamine or ammonia being present in an amount of from 0.5 to 20% by weight on the total solids content of the mixture, to a shapable dough obtained by this process, to the preparation of silica-alumina extrudates therefrom and to their use as catalyst carriers in hydrocarbon conversion or hydrocarbon synthesis reactions.

**EP 0 313 163 A1**

## SILICA-ALUMINA EXTRUDATES

The invention relates to the preparation of silica-alumina extrudates, to the preparation of a shapable dough for silica-alumina extrudates, to a shapable dough for silica-alumina extrudates and to the preparation of calcined silica-alumina extrudates and to their use.

5 In European patent application (publication) 167 324 is disclosed a method for the preparation of a silica extrudate whereby a particulate silica is mixed with water and an alkali metal compound to prepare a mixture which is extruded. However, the use of an alkali metal makes it necessary that the extruded silica must be soaked in a solution of ammonium nitrate and nitric acid to remove the alkali metal. The same applies to silicas containing another refractory oxide, such as alumina, according to the above-mentioned  
10 European patent application (publication) 167,324.

Applicant has found that this purification process may be obviated by using an alkanolamine or ammonia in the preparation of a dough from which silica-alumina extrudates can be obtained.

The invention therefore relates to a process for the preparation of a shapable dough which comprises mixing and kneading a particulate silica-alumina with water and with an alkanolamine or ammonia to obtain  
15 a mixture having a total solids content of from 25 to 60% by weight, the alkanolamine or ammonia being present in an amount of from 0.5 to 20% by weight on the total solids content of the mixture.

The invention further relates to a process for the preparation of silica-alumina extrudates which comprises mixing and kneading a particulate silica-alumina with water and with an alkanolamine or ammonia to obtain a mixture having a total solids content of from 25 to 60% by weight, the alkanolamine or ammonia  
20 being present in an amount of from 0.5 to 20% by weight on the total solids content of the mixture and extruding the mixture.

The invention further relates to a process for manufacturing calcined silica-alumina extrudates which comprises extruding a shapable dough into silica-alumina extrudates and drying and calcining the silica-alumina extrudates to a final temperature of between 300 °C and 1000 °C, and to calcined silica-alumina  
25 extrudates obtained by this process.

The silica-alumina to be used in the process according to our invention is silica-alumina obtained by reacting a silicate, preferably sodium- or potassium silicate, with an acid in the presence of an aluminium compound. Preferred is the washed silica-alumina filter cake.

When silica-alumina gel is gradually heated to a higher temperature it loses water. Heating during  
30 longer times above 100 °C results in that the water content decreases to about 5% by weight. The water content of the silica-alumina is determined by weight loss on ignition (LOI). A sample is weighed and then placed in a muffle furnace where it is heated at 1000 °C for 2 hours. After heating the sample is again weighed. The difference in weights represents the LOI or the amount of water present in the silica-alumina. When silica-alumina has been calcined, at e.g. 500 °C, it seems less suitable for use in the extrusion  
35 process. However silica-alumina gels which have been spray dried are very suitable.

The total solids content of the mixture of silica-alumina, ammonia or alkanolamine and water ranges from 25 to 60% by weight, preferably from 30 to 45% by weight and more preferably from 35 to 40% by weight, in order to obtain an extrudable mixture.

The amount of alkanolamine or ammonia ranges from 0.5 to 20% by weight, preferably from 2 to 15%  
40 by weight, more preferably from 3 to 10% by weight calculated on the total solids content.

To improve the flux properties in the extruder the mixture may also comprise a polyelectrolyte, such as Nalco 7879 (obtained from Nalco). The mixture (with or without polyelectrolyte) can readily be extruded e.g. over the metal die-plate of the Bonnot-extruder. Cylindrical extrudates can be prepared, but other forms may be prepared as well, such as mentioned in US patent specification 4,028,227. It is possible to prepare  
45 silica-alumina with a surface area of more than 350 m<sup>2</sup>/g.

The alkanolamines to be used in the process according to the invention may be mono-, di- or trialkanolamines. Preferred are monoalkanolamines, such as those containing 2 to 10 carbon atoms, e.g. ethanolamine, propanolamine, hexanolamine, nonanolamine and decanolamine. Other examples are diethanolamine and triethanolamine.

50 It is possible prior to extrusion to admix titanium dioxide or zirconium dioxide to the composition. This is advantageous when the silica-alumina is used as carrier and the titanium and zirconium are the effective catalyst ingredients.

The extruded silica-aluminas may be suitably used, for example, as carriers for catalysts, which are normally used in hydrocarbon conversion, like hydrodemetallization of heavy hydrocarbon oils, in hydrocarbon synthesis reactions, in the epoxidation of olefinically unsaturated compounds with organic hydroperox-

ides, in the hydrations of olefinically unsaturated compounds to produce the corresponding alkanols and in the purification of exhaust gases.

5 EXAMPLE

A mixture was prepared having the following composition:

	<b>silica-alumina</b>	
10	(ex Crossfield, 25 %w Al <sub>2</sub> O <sub>3</sub> )	1040 g (solids 800 g)
	<b>ethanolamine</b>	40 g
	<b>water (demineralized)</b>	<u>920 g</u>
15	<b>total</b>	<b>2000 g (LOI is 60%)</b>

The mixture was prepared by adding the ethanolamine and water to the silica-alumina and the mixture was kneaded for 45 min. The total kneaded mixture was extruded. The obtained extrudates (diameter 1.5 mm) were dried at 120 °C for 2 h, broken to pieces of about 4 to 5 mm and calcined at 500 °C for 2 h. The silica-alumina extrudate had the following properties:

BET surface area 379 m<sup>2</sup>/g  
 pore volume 0.91 ml/g (mercury intrusion)  
 bulk crushing strength 0.62 MPa.

25 **Claims**

- 30 1. A process for the preparation of a shapable dough which comprises mixing and kneading a particulate silica-alumina with water and with an alkanolamine or ammonia to obtain a mixture having a total solids content of from 25 to 60% by weight, the alkanolamine or ammonia being present in an amount of from 0.5 to 20% by weight on the total solids content of the mixture.
2. A process according to claim 1 wherein the silica-alumina is obtained by reacting a silicate with acid in the presence of an aluminium compound.
- 35 3. A process according to claim 2 wherein silica-alumina filter cake is used.
4. A process according to any one of the claims 1-3, wherein the total solids content is from 30 to 45% by weight, preferably 35 to 40% by weight.
5. A process according to any one of the claims 1-4, wherein the alkanolamine or ammonia is present in an amount of from 3 to 10% by weight on the total solids content.
- 40 6. A process according to any one of the claims 1-5, wherein a polyelectrolyte is admixed into the mixture.
7. A process according to any one of the claims 1-6, wherein titanium dioxide or zirconium dioxide is admixed.
8. A process for the preparation of silica-alumina extrudates from a shapable dough according to claim 1, which comprises mixing and kneading a particulate silica-alumina with water and with an alkanolamine or ammonia to obtain a mixture having a total solids content of from 25 to 60% by weight, the alkanolamine or ammonia being present in an amount of from 0.5 to 20% by weight on the total solids content of the mixture and extruding the mixture.
- 45 9. A process for manufacturing calcined silica-alumina extrudates which comprises drying and calcining the silica-alumina extrudates prepared by the process according to claim 8, to a final temperature of between 300 °C and 1000 °C.
- 50 10. Use of silica-alumina extrudates prepared by a process according to claim 9 as catalyst carriers in hydrocarbon conversion or hydrocarbon synthesis reactions.



DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A	US-A-4 542 118 (NOZEMACK et al.) ----		B 01 J 37/00
A	US-A-4 174 301 (CHOCA et al.) ----		B 01 J 32/00
A	US-A-4 264 474 (ALAFANDI et al.) ----		B 01 J 21/12
A	FR-A-2 154 905 (ENGELHARD MINERALS & CHEMICALS CORP.) ----		
A	US-A-3 442 821 (L. HILFMAN) ----		
D,A	EP-A-0 167 324 (MOBIL OIL CORP.) -----		
			<b>TECHNICAL FIELDS SEARCHED (Int. Cl.4)</b>
			B 01 J
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 13-01-1989	Examiner LO CONTE C.
<b>CATEGORY OF CITED DOCUMENTS</b> X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ..... & : member of the same patent family, corresponding document	