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microspheres is achieved by minimizing the amount of the reactive alumina in the kaolin microsphere by calcination at elevated temperatures. Mixing the calcined kaolin microspheres with a silica source and a seed solution used for in-situ FCC Y synthesis and heating results in growth of ZSM-5 crystals on the microsphere. The in-situ ZSM-5 has use as an FCC additive and catalyst for fine chemical processes such as organic compound manufacture.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is an XRD pattern of an as crystallized ZSM-5-containing microsphere formed by the process of this invention.

DETAILED DESCRIPTION OF THE INVENTION

Preparation of the fluid cracking additive catalyst, in accordance with this invention, involves an initial step of preparing microspheres comprising hydrous kaolin, metakaolin, kaolin calcined undergone through characteristic exothermic reaction, or mixtures of the kaolin forms. Optionally, colloidal silica, silica sol or sodium silicate binder can be added. The microspheres are calcined to convert any hydrous kaolin and metakaolin that may be present to spinel and/or mullite. In case where hydrous kaolin and metakaolin are not present, high calcination temperature may not be required. It is important that the microspheres prior to crystallization contain only a minimum of reactive alumina. Accordingly, the calcined microspheres will have a metakaolin content that is less than 10 wt. %. Preferably the metakaolin content in the calcined microspheres is less than 5 wt. %. Spinel and mullite contain little reactive alumina, which is determined by the amount of alumina solublized in a 1/1 hydrochloric acid/water solution following a thirty-minute digestion at 115° C.

The initial microspheres are made by spray drying a feed mixture containing hydrated kaolin, metakaolin, or kaolin calcined through the characteristic exothermic reaction and optionally colloidal silica and/or silica sol and/or sodium silicate binder. Mixtures of the kaolin forms can also be used. Enhancing the silica level in the preformed microsphere by including silica-rich components or using more silicate binder increases the overall reactive $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio, resulting in an increased level of crystallized ZSM-5. If a silicate binder is used such as sodium silicate, and if desired, sodium in the microspheres can be washed out at low pH, e.g., pH of 3. The spray dried microspheres are washed and then calcined to form precursor porous microspheres in which any of the hydrous kaolin and metakaolin is converted to spinel or mullite. The amount of metakaolin present in the calcined precursor microspheres needs to be minimized, i.e. less than 10%, to provide the desired reactive $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio and allow formation of ZSM-5 crystals. Typically, the calcined precursor microspheres will have a BET surface area of less than 200 m^2/g .

In an alternative method of forming a microsphere with a reduced reactive alumina content, the process of acid leaching a metakaolin as described in EP 068,817 can be used. According to the process as described therein, a method of manufacturing a crystalline zeolite of the ZSM family comprises the initial step of treating an aluminosilicate such as metakaolin with a strong acid at a temperature and for a time sufficient to extract at least part of the aluminum oxide content of the aluminosilicate and increase the molar ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ in the aluminosilicate to a value not less than 10:1. The acid used preferably has a pK_a value not greater

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than 2 and most preferably has a pK_a value of less than 0. Suitable acids include hydrochloric acid, sulphuric acid, nitric acid, and orthophosphoric acid. The acid should be used at a concentration of at least 2M, preferably at least 5M, and most preferably at least 7M. The optimum acid concentration depends upon the weight ratio of acid solution to dry aluminosilicate and upon the type of acid used and thus the nature of the aluminum salt formed and its solubility in the acid solution. The weight ratio of acid solution to dry aluminosilicate is preferably at least 5:1. The acid treatment is preferably performed at a temperature in the range of from 50° C. to 120° C. for at least 1 hour, and under conditions such that the molar ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ in the acid-treated aluminosilicate is in the range 10–200:1. Usually, after the acid treatment the molar ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ in the aluminosilicate is in the range 10–50:1.

The precursor microspheres, having a minimum of reactive alumina achieved either by high temperature calcination of kaolin or acid leaching of metakaolin, are reacted with zeolite Y seed solution and an alkaline sodium silicate solution. The zeolite Y seed solution is one intended for use in initiating crystallization of synthetic crystalline zeolite of the Y-type. ZSM-5 seeds are not used in the reaction.

Preparation of zeolite Y seed solution While it is useful to use crystallized zeolite Y seeds in this invention, the zeolite Y seed solution is most usefully obtained by processes disclosed in U.S. Pat. No. 4,493,902 and U.S. Pat. No. 4,631,262, the entire contents of which are herein incorporated by reference. As disclosed in U.S. Pat. No. 4,631,262, appropriate quantities of sodium silicate, sodium aluminate and sodium hydroxide are mixed, preferably in a controlled manner, hereinafter described, heating the resulting mixture for a time sufficient for the seeds to mature but insufficient for cloudiness to occur, and thereafter adding to the matured solution a portion of the sodium silicate reactant that would normally be included in the reaction slurry including the porous microspheres of calcined kaolin. The sodium silicate added to the matured seed solution is preferably at ambient temperature when it is added to the solution. The amount of sodium silicate solution added to the solution of matured clear seeds is effective to result in a seed solution which will maintain its clarity when aged for 48 hours or longer (without cooling). In effect, enrichment of a clear solution of matured seeds with sodium silicate functions to quench the undesirable reaction(s) that may take place and which would result in undesired cloudiness. The seed solution is amorphous and does not exhibit any detectable crystallinity by x-ray diffraction.

A solution of matured seeds which has become clouded or gelled can be made clear by adding additional sodium silicate solution, the amount of sodium silicate solution being effective to assure that the previously clouded or gelled solution will maintain its clarity when aged for 48 hours or longer without cooling. In this case, the sodium silicate enriched seed mixture is optionally, but preferably, heated and then permitted to age at ambient temperature. Heating after addition of sodium silicate is preferred because clarification will take place in a shorter time.

As used herein, the terms “solution of zeolite seed” and “zeolite initiator” shall include any aqueous solution containing silica, alumina and soda that either allows a zeolite Y crystallization process that would not occur in the absence of the seed material or shortens significantly the zeolite Y crystallization process that would occur in the absence of the seed material. Again, the zeolite Y seed solution as described above does not contain crystalline zeolite Y.