PROCESS FOR THE REGENERATION OF ZEOLITIC CATALYSTS

The present invention relates to a process for the regeneration of a zeolitic alkylation or transalkylation catalyst, at least partially exhausted, and comprises subjecting said exhausted catalyst to heat treatment with an aromatic hydrocarbon.

More specifically, the process of the present invention is useful for regenerating exhausted zeolitic catalysts which derive from preparation processes of monoalkylated aromatic hydrocarbons by the alkylation of an aromatic hydrocarbon substrate with a suitable alkylating agent selected from C_2-C_4 olefins, isopropanol and mixtures of isopropanol with propylene, or by the transalkylation of an aromatic hydrocarbon substrate with one or more polyalkylaromatic hydrocarbons, said alkylation or transalkylation processes being carried out in at least partially liquid phase and in the presence of a catalyst of zeolitic nature.

The regeneration of these exhausted catalysts accord-

ing to the present invention comprises treatment with an aromatic hydrocarbon effected in at least partially liquid phase and at a temperature equal to or higher than that at which the alkylation or transalkylation process was carried out.

It has been known for a long time that the alkylation of aromatic hydrocarbon substrates with C_2-C_4 olefins can be effectively carried out by the use of solid catalysts based on zeolites. In 1965 the preparation of cumene by the reaction of benzene with propylene using X or Y zeolite as catalyst, was described for the first time (Minachev, Kr. M., et al, Neftekhimiya 5 (1965) 676). The use of zeolites with a faujasitic structure for the alkylation of benzene with light olefins was subsequently described by Venuto et al. in J. Catal. 5, (1966) 81. U.S. 4,292,458 describes the use of ZSM-5 type zeolites for alkylating benzene with propylene. At present the best results in the alkylation of aromatic substrates with C_2-C_4 olefins, in particular benzene, in at least partially liquid phase, are obtained using beta zeolite as alkylation catalyst (EP 432,814, EP 687,500, EP 847,802).

The alkylation of benzene with isopropanol in the presence of Y zeolite is described in U.S. 5,015,786.

In U.S. 5,160,497, a dealuminated Y zeolite is used, with a molar ratio ranging from 8 to 70, for the alkylation

of benzene with propylene and isopropanol.

Preparations of monoalkylated aromatic hydrocarbons by the transalkylation of polyalkylated aromatic hydrocarbons with aromatic substrates in which zeolitic catalysts with small, medium and large pores are used, are described for example in U.S. 3,385,906, U.S. 4,169,111 and EP 308,097.

In particular, the transalkylation reaction of polyalkylated aromatic hydrocarbons can be suitably carried out in a step following the alkylation step of an aromatic hydrocarbon substrate with an olefin, operating on the polyalkylated products which are formed as by-products and are recovered downstream of the alkylation. The use of zeolitic catalysts for preparing monoalkylated aromatic hydrocarbons by the transalkylation of polyalkylated aromatic hydrocarbons in a step subsequent to the alkylation step is described in U.S. 3,385,906, U.S. 4,774,377, U.S. 4,168,111 and EP 308,097, where alkylation and transalkylation processes are combined to obtain better yields to monoalkylated aromatics.

EP 439,632, EP 687,500 and EP 847,802 describe the production of monoalkylated aromatic hydrocarbons from aromatic hydrocarbon substrates, not only by means of alkylation but also by means of transalkylation and a combined alkylation and transalkylation process, catalyzed by beta zeolite. In particular, the alkylation of benzene with eth-

ylene or propylene and the transalkylation of diethylbenzene or diisopropylbenzene with benzene are described.

Zeolites are materials characterized by a lattice structure in which the pore dimensions are of the same order of magnitude as that of the molecules of reagents and reaction products. The high selectivity of these materials in alkylation or transalkylation reactions, for example in the alkylation of benzene to cumene or ethylbenzene, or in the transalkylation of benzene with diethylbenzene or diisopropylbenzene, lies both in its particular acid characteristics and also in the shape-selectivity linked to the specific pore structure of the catalyst.

Owing to the limited channel dimensions in which the acid sites are situated and in which the molecules react, deactivation is a particularly significant phenomenon. It can be caused both by fouling of the single acid sites and also by physical blockage of the channels of the porous system; this is due to the formation of substances with a high molecular weight which obstruct the free passage of reagents and products and hinder the reaction process. The substances responsible for the deactivation of the catalyst are prevalently oligomers, polyalkylated products and polycondensed aromatic rings (anthracenes and higher aromatics) variously substituted. The combination of these substances is hereinafter referred to as pitches.

It is known that, once exhausted, the catalytic material can be partially or totally regenerated by means of thermal treatment at a high temperature (500-600°C) in an oxidative environment (oxygen or air). This in fact allows the combustion of the pitches present in the pores and the regeneration of the material under such conditions as to enable it to be used again in the reaction.

EP 0 353 813 describes the alkylation of aromatic hydrocarbons using alkylating agents containing from 2 to 20 carbon atoms, selected from olefins, alcohols, alkyl halides, esters, ethers and acetylene hydrocarbons. Synthetic or natural materials of the zeolitic or argillaceous type are used as catalysts, which after undergoing deactivation, can be regenerated by means of alternating cyclic washings effected with paraffins and alcohols. The pitches responsible for the deactivation are normally distinguished between soluble and insoluble products of which the latter cause additional weightiness and/or degradation with respect to the former, obstructing access (fully or partially) of the catalyst pores (M. Guisnet et al., in J. Catal. 106, 242-250, 1987 and J. Catal. 134, 286-298, 1992). The effect of the washings carried out in EP 353,813 relates to the dissolution of the polymeric compounds contained in the pitches.

It has now been surprisingly found that catalysts

based on zeolite used in alkylation or transalkylation processes, in particular used in alkylation reactions of aromatic substrates with an alkylating agent selected from C_2-C_4 olefins, isopropanol and mixtures of isopropanol and propylene, or used in transalkylation reactions of aromatic substrates with polyalkylaromatic hydrocarbons, once deactivated due to pitches, can be regenerated by means of heat treatment with an aromatic hydrocarbon.

This treatment not only removes the soluble component of the pitches, but is also capable of chemically degrading, by means of a reactive process, the insoluble pitches: the aromatic hydrocarbon in fact reacts with the pitches, probably by means of a series of alkylation and/or transalkylation reactions catalyzed by the zeolitic material itself, transforming the pitches into molecules characterized by a lower molecular weight, soluble in the aromatic hydrocarbon and, above all, capable of diffusing through the zeolitic pores.

An object of the present invention therefore relates to a process for the regeneration of a zeolitic catalyst at least partially exhausted, deriving from a preparation process of a monoalkylated aromatic compound by means of the alkylation of an aromatic hydrocarbon substrate with an alkylating agent selected from olefins containing from two to four carbon atoms, isopropanol and mixtures of isopro-

panol and propylene, or by means of the transalkylation of an aromatic hydrocarbon substrate with one or more polyalkylaromatic hydrocarbons, effected in the presence of the zeolitic catalyst and in at least partially liquid phase, said regeneration process comprising subjecting said exhausted catalyst to treatment with an aromatic hydrocarbon, in a liquid phase, at a temperature higher than that at which the alkylation or transalkylation process, from which the exhausted catalyst derives, was carried out, said temperature being comprised between 150°C and 290°C.

The aromatic hydrocarbon used for the regenerating treatment of the exhausted catalyst can be selected from benzene, toluene, naphthalene and their mixtures.

A preferred aspect of the present invention is that the aromatic hydrocarbon used for the regenerating treatment is equal to the aromatic substrate of the alkylation process from which the exhausted catalyst derives, or is equal to the aromatic substrate of the transalkylation process from which the catalyst to be regenerated derives.

The temperature at which the regenerating treatment can be effected ranges from 150 to 290°C, preferably from 200 to 290°C. The treatment is carried out for a time ranging from 0.1 to 60 hours, preferably from 15 to 45 hours, and at a pressure ranging from 5 to 50 bars, preferably from 20 to 40 bars.

The regeneration process is preferably carried out at a temperature which is higher than that of the alkylation or transalkylation process from which the exhausted catalyst derives.

Exhausted zeolitic catalysts which can be subjected to regeneration treatment according to the present invention are those containing a zeolite selected from beta zeolite, Y zeolite, mordenite, ZSM-12, MCM-22, and are preferably those containing beta zeolite.

The alkylation process, from which these exhausted catalysts derive, can be all the known alkylation processes in which an aromatic hydrocarbon substrate is alkylated with an alkylating agent selected from a C_2-C_4 olefin, isopropanol and mixtures of isopropanol and propylene, in the presence of a zeolitic catalyst and in at least partially liquid phase. The aromatic substrate which is alkylated can be benzene, toluene, naphthalene or their mixtures, and is preferably benzene; the olefin can be ethylene or propylene.

In particular, exhausted catalysts containing Y zeolite deriving from the alkylation process of benzene with ethylene or propylene to give cumene or ethylbenzene described in U.S. 5,177,285, EP 521,554 and EP 485,683, exhausted catalysts containing MCM-22 zeolite deriving from the alkylation of benzene with C_2-C_4 olefins described in

U.S. 4,992,606, exhausted catalysts containing ZSM-12 zeolite or mordenite deriving from the alkylation of benzene with C_2-C_4 olefins as described in Rao B. S., et al. "Proceedings, 1st Tokyo Conference on Advanced Catalyst Science and Technology", Tokyo, July 1-5, 1990 (S. Yoshida et al., Eds), Vol. 1, 56, page 361, can be regenerated according to the method of the present invention. Y zeolite is described in U.S. 3,130,007, MCM-22 zeolite is described in EP 64,205.

Exhausted catalysts containing Y zeolite deriving from the alkylation process of benzene with propanol to give cumene described in U.S. 5,015,786 and exhausted catalysts containing dealuminated Y zeolite used in the alkylation of benzene with isopropanol and propylene described in U.S. 5,160,497, can be regenerated according to the method of the present invention.

According to a preferred aspect, catalysts containing beta zeolite used for the alkylation of benzene with ethylene to give ethylbenzene or for the alkylation of benzene with propylene to give cumene described in EP 432,814, EP 439,632, EP 629,599, EP 687,500 and EP 847,802, can be regenerated according to the method of the present invention. In particular, the catalytic compositions comprising beta zeolite described in EP 687,500 and EP 847,802 are catalytic compositions consisting of beta zeolite and an inor-

ganic ligand characterized by an extra-zeolite porosity consisting for a fraction of at least 25% of pores with a radius higher than 100 Å and, in the case of EP 847,802 also characterized by a total extra-zeolitic pore volume greater than or equal to 0.80 ml/g.

According to another preferred aspect, exhausted zeolitic catalysts can be regenerated according to the method of the present invention, deriving from a process for the alkylation of aromatic compounds by reaction of the aromatic compound of interest with isopropanol, alone or mixed with an olefin, consisting in carrying out said alkylation reaction in the presence of a catalytic composition based on zeolite, under mixed gas-liquid phase conditions or under completely liquid phase conditions at such temperature and pressures that the concentration of water in the liquid reaction phase is not higher than 8,000 ppm, regardless of the total content of water present in the reaction mixture. In this alkylation process, the aromatic compound is preferably benzene and the olefin, when present, is propylene, the zeolite is beta zeolite, preferably in acid form, described in U.S. 3,308,069. This beta zeolite can be mixed with suitable binding agents, such as for example, alumina, or catalytic compositions can be used, comprising beta zeolite described in EP 687,500 and EP 847,802, i.e. catalytic compositions consisting of beta zeolite and an inorganic

ligand characterized by an extra-zeolite porosity consisting, for a fraction of at least 25%, of pores with a radius higher than 100 Å and, in the case of EP 847,802 also characterized by a total extra-zeolitic pore volume greater than or equal to 0.80 ml/g. This alkylation process is preferably carried out at a temperature ranging from 170 to 230°C, and at a reaction pressure ranging from 1 to 50 bars under mixed phase conditions using isopropanol and mixtures of isopropanol and propylene indifferently as alkylating agent. Experts in the field are able to define a priori - starting from the molar ratio benzene/isopropanol and propylene/isopropanol when propylene is also fed to the reaction section together with isopropylic alcohol - the temperature and pressure conditions which ensure that the concentration limit of water present in the liquid phase equal to about 8,000 ppm, regardless of the total quantity of water present in the reaction mixture and therefore regardless of the quantity of isopropanol fed to the reaction section, is respected.

The transalkylation processes from which exhausted catalysts which can be regenerated with the process of the present invention, derive, are all known transalkylation processes in which an aromatic substrate is transalkylated with one or more polyalkylaromatic hydrocarbons in the presence of a zeolitic catalyst and in at least partially

liquid phase. The aromatic substrate can be benzene, toluene, naphthalene or their mixtures, and is preferably benzene, the polyalkylaromatic hydrocarbon can be selected from diethylbenzene, optionally mixed with triethylbenzene, and diisopropylbenzene, optionally mixed with triisopropylbenzene.

In particular, exhausted catalysts containing Y zeolite deriving from the transalkylation process of benzene with diethylbenzene or diisopropylbenzene described for example in I.I. Lishchiner et al., React. Kinet. Catal. Lett., Vol. 23, Nrs. 3-4, 261-265 (1983), exhausted catalysts containing MCM-22 zeolite used in the transalkylation of polyalkylaromatics, such as for example the transalkylation of diisopropylbenzene described in U.S. 5,371,310, exhausted catalysts containing ZSM-12 zeolite or mordenite used in the transalkylation of polyalkylaromatics described in EP 308,097, can be regenerated according to the method of the present invention.

According to a preferred aspect, catalysts containing beta zeolite used for the transalkylation of diethylbenzene with benzene and diisopropylbenzene with benzene described in EP 432,814, EP 439,632, EP 629,599, EP 687,500 and EP 847,802, can be regenerated according to the method of the present invention.

The process of the present invention can be effected

by recovering the exhausted catalyst from the alkylation or transalkylation reactor and subjecting it to regenerating treatment with the pre-selected aromatic hydrocarbon in a specific reactor, but a preferred aspect of the present invention is that the regeneration process of the catalyst, at least partially exhausted, is effected in the same alkylation or transalkylation reactor, by feeding the aromatic hydrocarbon selected for the regenerating treatment, after suspending the feeding of the alkylation or transalkylation reagents. This embodiment is particularly convenient and preferred when the alkylation or transalkylation reactor is a continuous reactor, even more preferably a catalytic fixed bed continuous reactor.

When the regeneration process of the at least partially exhausted catalyst is carried out in the same alkylation or transalkylation reactor, a particularly preferred aspect of the present invention is to use, as aromatic hydrocarbon for the regenerating treatment, the same aromatic substrate used in the alkylation or transalkylation process, after suspending the feeding of the alkylating reagent or polyalkylbenzene, respectively, to the reactor. This embodiment is particularly convenient and preferred when the alkylation or transalkylation reactor is a continuous reactor, even more preferably a catalytic fixed bed continuous reactor. In practice, according to this particular embodi-

ment in continuous of the regeneration process of the present invention, when a zeolitic alkylation catalyst is exhausted, the feeding stream of the alkylating agent to the alkylation reactor is suspended, said alkylating agent being selected from C_2-C_4 olefins, isopropanol or mixtures of isopropanol and propylene, whereas the stream of aromatic substrate continues to be fed to the reactor, optionally raising the temperature of the catalytic bed, when it has been decided to carry out the regeneration treatment at a higher temperature than that of the alkylation process. When the regeneration process is concluded, the feeding of the alkylating agent is restarted to re-begin the alkylation process, after possible cooling of the catalytic bed. This particular embodiment is very useful in the case of the regeneration of an exhausted catalyst containing beta zeolite, Y zeolite or MCM-22 zeolite, preferably beta zeolite, deriving from the alkylation of benzene with ethylene to give ethylbenzene or of benzene with propylene to give cumene, or deriving from the alkylation of benzene with isopropanol, alone or mixed with propylene.

According to a particular embodiment in continuous of the regeneration process of the present invention, when an exhausted catalyst deriving from a transalkylation process is to be regenerated, the feeding polyalkylaromatic hydrocarbon stream to the transalkylation reactor is suspended,

whereas the stream of aromatic substrate continues to be fed to the reactor, optionally raising the temperature of the catalytic bed when it has been decided to carry out the regeneration treatment at a higher temperature than that of the transalkylation process. When the regeneration process is concluded, the feeding of the polyalkylated aromatic is restarted to re-begin the transalkylation process, after possible cooling of the catalytic bed. This particular embodiment is very useful in the case of the regeneration of an exhausted catalyst containing beta zeolite, Y zeolite or MCM-22 zeolite, preferably beta zeolite, deriving from the transalkylation of benzene with diethylbenzene, optionally mixed with triethylbenzene, or from the transalkylation of benzene with diisopropylbenzene, optionally mixed with triisopropylbenzene.

In all cases in which the regeneration is carried out in the same alkylation or transalkylation reactor, and said reactor is in continuous, a WHSV preferably ranging from 1 to 20 h^{-1} is adopted, even more preferably from 2 to 8 h^{-1}.

In accordance with what is specified above, a further aspect of the present invention relates to an alkylation process in continuous, in the presence of a zeolitic catalyst, preferably in a fixed bed reactor, of an aromatic substrate with an alkylating agent selected from olefins containing from 2 to 4 carbon atoms, isopropanol and mix-

tures of isopropanol and propylene, with cyclic regeneration of the catalyst, comprising the following steps:

a) alkylation of a feeding of aromatic substrate with a feeding of alkylating agent, carried out in at least partially liquid phase and in the presence of a zeolitic catalyst, until the catalyst shows at least partial deactivation;

(b) suspension of the feeding of the alkylating agent and treatment of said deactivated catalyst with the feeding of the aromatic substrate alone, in liquid phase and at a temperature higher than the alkylation temperature of step a), said temperature being comprised between 150°C and 290°C, until the catalyst has been regenerated;

c) re-establishment of the temperature conditions used in the alkylation in step a) when the regeneration has been carried out at a temperature higher than that of the alkylation step, and re-starting of the feeding of the alkylating agent.

The regeneration process of step b) is preferably carried out at a WHSV ranging from 1 to 20 hours^{-1}, preferably from 2 to 8 hours^{-1}. The temperature of this step preferably ranges from 200 to 290°C.

The aromatic substrate is preferably benzene and, when the alkylating agent is an olefin, said olefin is preferably selected from ethylene and propylene. The zeolitic catalyst preferably contains a zeolite selected from beta

zeolite and Y zeolite, and is preferably beta zeolite. The reaction conditions of step a) are those described in literature and known to experts in the field or those described above relating to the alkylation of aromatic substrates, in the presence of beta zeolite, with isopropanol, alone or mixed with propylene.

In accordance with what is specified above, a further aspect of the present invention relates to a transalkylation process in continuous, in the presence of a zeolitic catalyst, preferably in a fixed bed reactor, of an aromatic substrate with one or more polyalkylaromatics, with cyclic regeneration of the catalyst, comprising the following steps:

a) transalkylation of a feeding of aromatic substrate with a feeding of polyalkylaromatic hydrocarbon, carried out in at least partially liquid phase and in the presence of a zeolitic catalyst, until the catalyst shows at least partial deactivation;

(b) suspension of the feeding of the polyalkylaromatic hydrocarbon and treatment of said deactivated catalyst with the feeding of the aromatic substrate alone, in liquid phase and at a temperature higher than the transalkylation temperature of step a), said temperature being comprised between 150°C and 290°C, until the catalyst has been regenerated;

c) re-establishment of the temperature conditions used in

the transalkylation in step a) when the regeneration has been carried out at a temperature higher than that of the transalkylation step, and re-starting of the feeding of the polyalkylaromatic.

The regeneration process of step b) is preferably carried out at a WHSV ranging from 1 to 20 h^{-1}, preferably from 2 to 8 h^{-1}. The temperature of this step preferably ranges from 200 to 290°C.

The aromatic substrate is preferably benzene and the aromatic hydrocarbon is preferably selected from diethylbenzene, optionally mixed with triethylbenzene, and diisopropylbenzene, optionally mixed with triisopropylbenzene. The zeolitic catalyst preferably contains a zeolite selected from beta zeolite and Y zeolite, and is preferably beta zeolite. The process conditions of step (a) are those described in the prior art and are known to experts in the field.

The regeneration of exhausted catalysts according to the present invention and in accordance with what is described above, is conveniently used also in the case of catalysts deriving from a preparation process of a monoalkylated aromatic hydrocarbon comprising the following steps:

1) alkylation of a feeding of aromatic substrate with a feeding of an alkylating agent selected from C_2-C_4 olefins,

isopropanol and mixtures of isopropanol and propylene, carried out in at least partially liquid phase and in the presence of a zeolitic catalyst;

2) separation of the product obtained in (a) into a fraction containing the aromatic substrate (b), a fraction containing a monoalkylated aromatic hydrocarbon and (c) a fraction containing polyalkylated aromatic hydrocarbons,

3) transalkylation of the fraction containing polyalkylated aromatic hydrocarbons with the aromatic substrate, carried out in at least partially liquid phase and in the presence of a zeolitic catalyst.

In this multi-stepped process the regeneration of the exhausted catalysts can be carried out by contemporaneously suspending the feeding of both the alkylating reagent and polyalkylaromatic hydrocarbon, and letting the aromatic substrate flow alone until the catalysts have been regenerated, or, preferably, the regeneration of the catalyst of step (a) and the catalyst of step (b) are carried out independently.

EXAMPLE 1

An alkylation test of benzene with propylene to give cumene is carried out using an experimental apparatus consisting of an AISI316 fixed bed micro-pilot reactor, with an internal diameter of 1 cm., a total length of 8.5 cm, tanks for the benzene and propylene in the feeding, dosage

pumps for the feeding of the two reagents in liquid phase, an automatic system for the temperature and pressure control, for discharging the effluent from the reactor and for analysis of the feed and product. The catalyst used in this test is a catalyst based on beta zeolite similar to that prepared and described in example 4 of patent application EP 0 847 802. 4.5 g of said catalyst, sieved into granules having dimensions equal to 20-40 mesh, and 11.5 g of inert material, are charged into the reactor, obtaining a homogeneous catalytic bed having a height equal to 8.5 cm. Benzene and propylene are fed, at a temperature of 150°C, a pressure of 30 barg, a WHSV of 19.6 g/g/hour and a benzene/propylene ratio of 6 m/m, obtaining a weight percentage of cumene in the effluent of 19.6. The test is prolonged until the concentration of cumene in the effluent drops to below 5% by weight (3.72%). At this point the regeneration procedure of the exhausted catalyst is initiated:

- the feeding of propylene is interrupted whereas the feeding of benzene remains unaltered (WHSV = 19.6 g/g/hour);
- the catalytic bed is heated to a temperature of 220°C (at a rate of 0.6°C/min);
- the above temperature is maintained for 3 hours;
- the catalytic bed is cooled to a temperature of

150°C.

At the end of the regeneration procedure described above, the feeding of propylene is re-started, the alkylation process is re-activated as described above, and a weight percentage of cumene is obtained in the effluent equal to 19.51. The test is prolonged until the concentration of cumene in the effluent drops to 6.20% by weight. At this point a regeneration procedure of the exhausted catalyst analogous to that described above, is initiated. At the end of this second regeneration, the alkylation process is re-started, obtaining a weight percentage of cumene in the effluent equal to 19.65.

EXAMPLE 2

An alkylation test of benzene with propylene to give cumene is carried out using an experimental apparatus consisting of an AISI316 fixed bed micro-pilot reactor, with an internal diameter of 1 cm., a total length of 8.5 cm, tanks for the benzene and propylene in the feeding, dosage pumps for the feeding of the two reagents in liquid phase, an automatic system for the temperature and pressure control, for discharging the effluent from the reactor and for the analysis of the feed and product. The catalyst used in this test is a catalyst based on beta zeolite similar to that prepared and described in example 4 of patent application EP 0 847 802. 4.5g of said catalyst, sieved into gran-

ules having dimensions equal to 20-40 mesh, and 11.5 g of inert material, are charged into the reactor, obtaining a homogeneous catalytic bed having a height equal to 8.5 cm. Benzene and propylene are fed, at a temperature of 150°C, a pressure of 30 barg, a WHSV of 19.6 g/g/hour and a benzene/propylene ratio of 6 m/m, obtaining a weight percentage of cumene in the effluent of 19.44. The test is prolonged until the concentration of cumene in the effluent drops to below 5% by weight (3.04%). At this point the regeneration procedure of the exhausted catalyst is initiated:

- the feeding of propylene is interrupted
- the flow-rate of the benzene feeding is reduced to a value of WHSV = 4.0 g/g/hour
- the catalytic bed is heated to a temperature of 220°C (at a rate of 0.6°C/min);
- the above temperature is maintained for 24 hours;
- the catalytic bed is cooled to a temperature of 150°C.

At the end of the regeneration procedure described above, the original flow-rate of benzene is re-established and also the feeding of propylene, the alkylation process is re-activated as described above, and a weight percentage of cumene is obtained in the effluent equal to 19.31. The test is prolonged until the concentration of cumene in the

effluent drops to 4.42% by weight. At this point a regeneration procedure of the exhausted catalyst analogous to that described above, is initiated. At the end of this second regeneration, the alkylation process is re-started, obtaining a weight percentage of cumene in the effluent equal to 19.28.

EXAMPLE 3

An alkylation test of benzene with propylene to give cumene is carried out using an experimental apparatus consisting of an AISI316 fixed bed micro-pilot reactor, with an internal diameter of 1.2 cm., a total length of 22 cm, tanks for the benzene and propylene in the feeding, dosage pumps for the feeding of the two reagents in liquid phase, an automatic system for the temperature and pressure control, for discharging the effluent from the reactor and for the analysis of the feed and product.

The catalyst used in this test is a commercial Y zeolite (called 330 HUA, of Tosoh Corporation).

The conditions for the alkylation reaction are the following:

Temperature at the inlet =	150°C
Pressure =	38 barg
WHSV =	20 g/g/h
[Benzene]/[Propylene] =	7 m/m

1.2 g of catalyst (obtained first by forming tablets

of catalyst in powder form and then grinding and sieving into granules having dimensions equal to 20-40 mesh) and 30 g of inert material are charged into the reactor, obtaining a homogeneous catalytic bed having a height equal to 22 cm. The feeding of the reagents is started, obtaining a weight percentage of cumene in the effluent equal to 13.71.

When the concentration of cumene in the effluent drops to below 5% by weight (2.9%), the following regeneration procedure is initiated:

- the feeding of propylene is interrupted
- the catalytic bed is heated to a temperature of 200°C;
- the above temperature is maintained for 5 hours;
- the catalytic bed is cooled to a temperature of 150°C.

At the end of the regeneration procedure described above, the feeding of propylene is re-started, the alkylation process is re-activated as described above, and a weight percentage of cumene is obtained in the effluent equal to 13.61. When the concentration of cumene in the effluent drops to below 5% by weight (2.1%), a regeneration procedure analogous to that described above, is initiated. At the end of the regeneration, the alkylation process is re-started, obtaining a weight percentage of cumene in the effluent equal to 13.55.

EXAMPLE 4 (comparative)

An alkylation test of benzene with propylene to give cumene is carried out using a catalyst based on beta zeolite and the experimental apparatus described in example 1.

The reaction conditions during the test are the following:

Temperature at the inlet =	150°C
Pressure =	30 barg
WHSV =	20.0 g/g/h
[Benzene]/[Propylene] =	6 m/m

4.5 g of the catalyst of example 1, ground and sieved into granules having dimensions equal to 20-40 mesh, and 11.5 g of inert material are charged into the reactor, obtaining a homogeneous catalytic bed having a height equal to 8.5 cm. The reagents are fed and a weight percentage of cumene is obtained in the effluent equal to 19.7.

The test is prolonged and when the concentration of cumene in the effluent drops to below 5% (1.01%) the following regeneration procedure of the exhausted catalyst is initiated:

- the feeding of propylene and benzene is interrupted
- the system is flushed with nitrogen
- n-hexane is fed with the same flow-rate used for the benzene in the alkylation phase

- the catalytic bed is heated to a temperature of 200°C (at a rate of 0.6°C/min);
- the above temperature is maintained for 3 hours;
- the catalytic bed is cooled to a temperature of 150°C.

At the end of the regeneration procedure described above, the system is flushed again with nitrogen, the feeding of benzene and propylene and the alkylation test are re-started as described above, obtaining a weight percentage of cumene in the effluent of 1.66. A second regeneration procedure is effected, in the same way as described before, using cyclohexane instead of n-hexane. At the end of the regeneration procedure described, the system is flushed again with nitrogen and the feeding of benzene and propylene and alkylation test are re-started as described above, obtaining a weight percentage of cumene in the effluent of 0.93.

CLAIMS

1) A process for the regeneration of a zeolitic catalyst at least partially exhausted, deriving from a preparation process of a monoalkylated aromatic compound by means of the alkylation of an aromatic hydrocarbon substrate with an alkylating agent selected from olefins containing from two to four carbon atoms, isopropanol and mixtures of isopropanol and propylene, or by means of the transalkylation of an aromatic substrate with one or more polyalkylated aromatic hydrocarbons, effected in the presence of a zeolitic catalyst and in at least partially liquid phase, said regeneration process comprising subjecting the exhausted catalyst to treatment with an aromatic hydrocarbon, in a liquid phase, at a temperature higher than that at which the alkylation or transalkylation process, from which the exhausted catalyst derives, was carried out, said temperature being comprised between 150°C and 290°C.

2) The process according to claim 1, wherein the aromatic hydrocarbon used for the regeneration treatment is selected from benzene, toluene, naphthalene and their mixtures.

3) The process according to claim 1, carried out at a temperature ranging from 150 to 290°C, at a pressure ranging from 5 to 50 bars and for a time ranging from 0.1 to 60 hours.

4) The process according to claim 3, carried out at a temperature ranging from 200 to 290°C, at a pressure ranging from 20 to 40 bars and for a time ranging from 15 to 35 hours.

5) The process according to claim 1, wherein the zeolitic catalyst is a catalyst containing a zeolite selected from beta zeolite, Y zeolite, mordenite, ZSM-12, MCM-22.

6) The process according to claim 5, wherein the zeolite is beta zeolite.

7) The process according to one of the claims from 1 to 6, wherein the exhausted catalyst derives from an alkylation process of an aromatic substrate with an alkylating agent selected from olefins containing from two to four carbon atoms, isopropanol and mixtures of isopropanol and propylene, carried out in at least partially liquid phase.

8) The process according to claim 7, wherein the aromatic substrate is benzene, toluene, naphthalene or their mixtures.

9) The process according to claim 8, wherein the aromatic substrate is benzene.

10) The process according to claim 7, wherein the alkylating agent is ethylene or propylene.

11) The process according to claim 7, wherein the exhausted catalyst is based on beta zeolite and derives from

an alkylation process of benzene with an alkylating agent selected from ethylene, propylene, isopropanol and mixtures of isopropanol with propylene.

12) The process according to claim 7, wherein the aromatic hydrocarbon used for the regenerating process is equal to the aromatic substrate of the alkylation process.

13) The process according to claim 7, carried out in the same alkylation reaction.

14) The process according to claim 13, wherein the reactor is a continuous reactor.

15) The process according to claim 14, wherein the reactor is a fixed bed continuous reactor.

16) The process according to claim 12 and 15, wherein the regeneration treatment is carried out in continuous using as aromatic hydrocarbon the same aromatic substrate stream as the alkylation process.

17) The process according to claim 16, wherein an exhausted catalyst based on beta zeolite deriving from an alkylation process of benzene with an alkylating agent selected from ethylene, propylene, isopropanol and mixtures of isopropanol with propylene, is regenerated in the same alkylation reactor using the benzene stream.

18) The process according to one of the claims from 1 to 6, wherein the exhausted catalyst derives from a transalkylation process of an aromatic hydrocarbon sub-

strate with a polyalkylated aromatic hydrocarbon, carried out in at least partially liquid phase.

19) The process according to claim 18, wherein the aromatic substrate is benzene, toluene, naphthalene or their mixtures.

20) The process according to claim 18, wherein the aromatic substrate is benzene.

21) The process according to claim 18, wherein the polyalkylated aromatic hydrocarbon is diisopropylbenzene, optionally mixed with triisopropylbenzene, or diethylbenzene, optionally mixed with triethylbenzene.

22) The process according to claim 18, wherein the exhausted catalyst is based on beta zeolite and derives from a transalkylation process of benzene with diisopropylbenzene, optionally mixed with triisopropylbenzene, or diethylbenzene, optionally mixed with triethylbenzene.

23) The process according to claim 18, wherein the aromatic hydrocarbon used for the regenerating process is equal to the aromatic substrate of the transalkylation process.

24) The process according to claim 18, carried out in the same alkylation reactor.

25) The process according to claim 24, wherein the reactor is a continuous reactor.

26) The process according to claim 25, wherein the

reactor is a fixed bed continuous reactor.

27) The process according to claim 23 and 26, wherein the regeneration treatment is carried out in continuous using as aromatic hydrocarbon the same aromatic substrate stream as the transalkylation process.

28) The process according to claim 27, wherein an exhausted catalyst based on beta zeolite deriving from a transalkylation process of benzene with diisopropylbenzene, optionally mixed with triisopropylbenzene, or diethylbenzene, optionally mixed with triethylbenzene, is regenerated in the same transalkylation reactor using the benzene stream.

29) An alkylation process in a continuous reactor of an aromatic substrate with an alkylating agent selected from olefins containing from 2 to 4 carbon atoms, isopropanol and mixtures of isopropanol with propylene, in the presence of a zeolitic catalyst, with cyclic regeneration of the zeolitic catalyst, comprising the following steps:

a) alkylation of a feeding of aromatic substrate with a feeding of alkylating agent, carried out in at least partially liquid phase and in the presence of the zeolitic catalyst, until the catalyst shows at least partial deactivation;

(b) suspension of the feeding of the alkylating agent and treatment of said deactivated catalyst with the feeding

of the aromatic substrate alone, in liquid phase and at a temperature higher than the alkylation temperature of step a), said temperature being comprised between 150°C and 290°C, until the catalyst has been at least partially regenerated;

c) re-establishment of the temperature conditions used in the alkylation in step a) when the regeneration has been carried out at a temperature higher than that of the alkylation step, and re-starting of the feeding of the alkylating agent.

30) The process according to claim 29, wherein the deactivated catalyst is based on beta zeolite, the aromatic substrate is benzene and the alkylating agent is selected from ethylene, propylene, isopropanol, mixtures of isopropanol with propylene.

31) A transalkylation process in a continuous reactor of an aromatic substrate with a polyalkylated aromatic hydrocarbon, in the presence of a zeolitic catalyst, with cyclic regeneration of the zeolitic catalyst, comprising the following steps:

a) transalkylation of a feeding of aromatic substrate with a feeding of polyalkylated aromatic hydrocarbon, carried out in at least partially liquid phase and in the presence of a zeolitic catalyst, until the catalyst shows at least partial deactivation;

(b) suspension of the feeding of the polyalkylaro-

matic hydrocarbon and treatment of said deactivated catalyst with the feeding of the aromatic substrate alone, in liquid phase and at a temperature higher than the transalkylation temperature of step a), said temperature being comprised between 150°C and 290°C, until the catalyst has been at least partially regenerated;

c) re-establishment of the temperature conditions used in the transalkylation in step a) when the regeneration has been carried out at a temperature higher than that of the transalkylation step, and re-starting of the feeding of the polyalkylated aromatic hydrocarbon.

32) The process according to claim 31, wherein the deactivated catalyst is based on beta zeolite, the aromatic substrate is benzene and the polyalkylated aromatic hydrocarbon is selected from diisopropylbenzene, optionally mixed with triisopropylbenzene, and diethylbenzene, optionally mixed with triethylbenzene.

33) The process according to claim 16, 29 or 31, wherein the regeneration is carried out at a WHSV ranging from 1 to 20 h^{-1}.

34) The process according to claim 33, wherein the regeneration is carried out at a WHSV ranging from 2 to 8 h^{-1}.

PROCESS FOR THE REGENERATION OF ZEOLITIC CATALYSTS

Abstract

The present invention relates to a process for the regeneration of a zeolitic alkylation or transalkylation catalyst, at least partially exhausted, and comprises subjecting said exhausted catalyst to heat treatment with an aromatic hydrocarbon.

In particular, the process of the present invention is useful for regenerating exhausted zeolitic catalysts which derive from preparation processes of monoalkylated aromatic hydrocarbons by the alkylation of an aromatic hydrocarbon substrate with an alkylating agent selected from C_2-C_4 olefins, isopropanol and mixtures of isopropanol with propylene, or by the transalkylation of an aromatic hydrocarbon substrate with one or more polyalkylaromatic hydrocarbons, said alkylation or transalkylation processes being carried out in at least partially liquid phase and in the presence of a catalyst of zeolitic nature.