Candidate's Answer – A (Chemistry)

The present invention relates to an alkylation process, and to further processes in which this alkylation process can be applied. The invention also relates to a catalyst particularly adapted for use in such processes, and to a method for producing the catalyst.

Akylation processes involving the alkylation of an alkylbenzene by an alkene or a conjugated diene are known (see D1).

However, a disadvantage of of such processes of such processes is that they typically result in a mixture of straight and branch-chained products.

This can be disadvantageous in processes where only the straight-chained product is desired, because the straight-chained product may need to be separated from the branched chain products - this can be difficult.

Therefore, the present invention aims to overcome the above disadvantage.

Accordingly, the present invention provides: <claim 1>
Accordingly, the present invention provides: <claim 11>
Accordingly, the present invention provides other indep claims: <-> <->

The process of claim 1 provides the surprising advantage that the alkylation process results in a greater ratio of straight-chained to branched-chain products, compared to the processes known in the art, eg D1.

This makes the process of claim 1 particularly suited to further processes of economic interest where mainly straight-chained products are required. All these advantages result from the use of the particular catalyst of claim 17.

One such further process is for the production of 2,6-DMN, which is in turn used to make PEN, which is in turn used to make plastic bottles.

Therefore in preferred aspects of the invention, the alkylation process is applied to the production of such products.

LETTER FROM THE APPLICANT

~~*As you are aware, we have substantial interests, through a joint venture, in the preparation of reusable plastic bottles.*~~ *A published set of experiments has shown that the most suitable plastic for making reusable bottles is polyethylenenaphthalate (PEN). A bottle that is going to be reused has to be cleaned and sterilised at high temperatures. Bottles made from PEN are much better able to withstand these high temperatures than bottles made from other known plastics.*

We have not yet been able to commercialise PEN bottles, because up to now the cost of making PEN has always been too high. The high cost of PEN follows directly from the difficulty in making the key precursor: 2,6-dimethylnaphthalene (2,6-DMN). A number of

synthetic routes to 2,6-DMN have been published. The known routes all have at le one of the following problems:

a) The route uses expensive precursors

b) The route is a multistage reaction, consisting of four or five reaction steps.

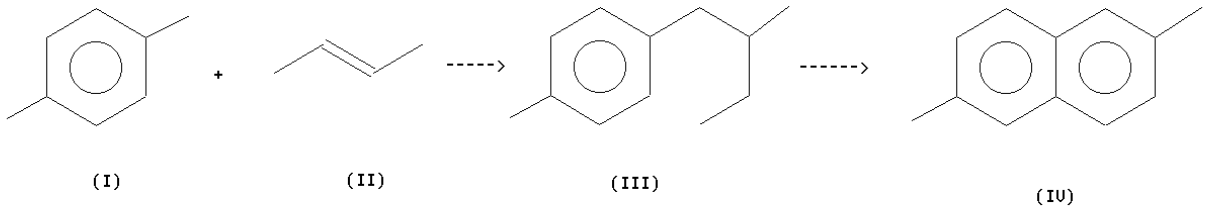
c) The reactions used are not selective and produce a lot of side products, which are typically very difficult to separate from 2,6-DMN.

We have succeeded in finding a way to manufacture 2,6-DMN by an economic and simple process which starts from a cheap precursor and is selective and involves a minimum number of steps. ~~On the following pages we have described our process in more detail. Please file a European patent application based on this information. If need be, more than one application may be filed. Copies of what we think is the closest state of the art are also provided.~~

~~The process we have developed comprises~~ In a preferred aspect, the process involves *the following steps:*

- *the reaction between para-xylene (p-xylene) (I) and butene (II) to produce p-(2-methylbutyl)-toluene (III)*
- *dehydrocyclisation of p-(2-methylbutyl)-toluene to produce 2,6-dimethylnaphthalene (2,6-DMN (IV)).*

A simplified illustration of the reaction scheme is presented below:



(I) (II) (III) (IV)

Each of the steps will now be described:

I. ***Preparation of p-(2-methylbutyl)-toluene (III)***

In the first step an alkylation reaction is performed in which p-xylene is reacted with butene. The alkylation reaction adds a butyl group to a methyl group on the xylene. This reaction can form products with either a straight side chain (in which case the reaction product is p-(n-pentyl)-toluene) or a branched side chain (in which case the product is the desired p-(2-methylbutyl)-toluene).

Depending on the precise catalyst used, the ratio between the branched and straight-chained products varies somewhat. It is very important in our reaction scheme to avoid as far as possible the formation of straight chained products such as p-(n-pentyl)-toluene. If significant amounts of p-(n-pentyl)toluene are formed, this compound has to be removed (e.g. by fractional crystallisation) before the dehydrocyclisation step. If p-(n-pentyl)toluene is present during the dehydrocyclisation reaction significant amounts of isomers of 2,6-DMN will be produced. It is very difficult to separate 2,6-DMN from these isomers.

In order to minimise the formation of straight-chained products the reaction has to be performed in the presence of a supported alkali metal catalyst. In principle all alkali metals can be used, it is however preferred for economic reasons to use sodium, potassium or a mixture of these two metals. The metals have to be used on a support. ~~The reaction my be performed with the alkali metal supported on standard supports. The highest~~ High *yields of p-(2-methylbutyl)-toluene (III) are obtained when the support itself is basic.*

We define a basic support to be a material, which desorbs carbon dioxide at a temperature higher than a standard alpha-alumina. The procedure for measuring this desorption temperature and the precise nature of the standard alpha-alumina to be used are set out in the patent US-A-1 000 000.

Particularly preferred basic supports are powdered sodium or potassium carbonate since when catalysts having these supports are used, virtually no p-(n-pentyl)-toluene will be formed. In this case no separation step is necessary.

A. Preparation of the catalyst

A supported alkali metal catalyst suitable for our reaction can be prepared by introducing the alkali metal and the support in a weight proportion of 1 part metal to 0.5 - 500 parts of support into a closed vessel containing an organic solvent under an inert atmosphere. The resulting mixture is stirred at high speed at a typically at temperature between 30 and 60°C for 1 to 5 hours. The organic solvent used is preferably one of the reactants.

Example

3 parts of metallic sodium and 97 parts of potassium carbonate were simultaneously charged into 200 parts of p-xylene. The mixture is heated to 50°C and stirred at high speed for 2 hours.

B. Preparation of p-(2-methylbutyl)-toluene

The reactants should be dry. If necessary, a drying step is to be included. The reaction system should be free of oxygen.

The reaction is usually performed at a temperature between 100 and 200°C. Below 100°C, the reaction is too slow. Above 200°C, the selectivity decreases. The preferred temperature range is from 110 to 180°C.

A reaction time of from 1 to 10 hours has typically been used.

The process can be operated continuously in a tubular reactor or discontinuously in a batch reactor. When the catalyst becomes less active, it can be taken out of the system and replaced.

Example

The sodium supported on potassium carbonate catalyst obtained in the example above (suspended in p-xylene) is introduced into a reactor kept at 120°C. Additional p-xylene is added to obtain a weight proportion p-xylene to catalyst of 10:1. Butene is then slowly bubbled through the reactor for 5 hours. The p-(2-methylbutyl)-toluene product is filtered from the catalyst. The product can be passed directly to the dehydrocyclisation step without further purification.

II. Dehydrocyclisation to 2,6-dimethylnaphthalene (IV)

This reaction is performed in the gas phase, using a solid catalyst. Many commercially available catalysts can be used. The most suitable catalysts are based on metals of the platinum group (for example platinum or palladium) supported on an oxide such as chromium oxide, alumina, silica or a zeolite. The reaction is well known in the literature, and it is not necessary to describe it in more detail. We have used catalysts comprising platinum supported on a zeolite in our experiments since these catalysts were available in our plant.

A. Preparation of the catalyst

A platinum on zeolite Y catalyst can be used. This catalyst may be prepared by any of the known processes. Typically the catalyst is prepared by impregnating the zeolite with a solution of a platinum compound until a paste is formed, extruding the paste as pellets, drying the pellets (a few hours at a temperature slightly above 100°C) and calcining the dried pellets (at least 3 hours in air at 500 to 600°C). The platinum content should be in the range 0.5 to 2.5% by weight of the catalyst.

B. Preparation of 2,6-DMN

The dehydrocyclisation process may be performed by passing a gas containing hydrogen and p-(2-methylbutyl)-toluene (III) at a temperature in the range of 150 to 400°C, preferably between 200 and 300°C over the catalyst. In order to avoid side reactions, an inert gas, such as nitrogen, carbon dioxide or steam is often added.

In order to make it simpler to uniformly transfer the solid starting material into t phase, it can be dissolved in a solvent such as an aromatic (benzene, toluene) o aliphatic hydrocarbon (hexane, heptane). 2,6-DMN can be condensed from the gas

Example

A platinum on zeolite catalyst was put into a 3 mm quartz tube. Then p-(2-methylbutyl)-toluene (III) and a 1:1 nitrogen:hydrogen mixture were introduced. The reaction conditions are: temperature 310°C, pressure 1 bar, contact time 0.8 sec. The yield of 2,6-DMN was 77.5%.

III. Purification of the product

The product obtained from the dehydrocyclisation contains some impurities, and can be purified by distillation.

~~*FAX FROM THE APPLICANT*~~

~~*URGENT!!!*~~

~~*Shortly after sending you the request for drafting the said application , the project leader informed me that additional tests have been done concerning the frist (alkylation) step of our process. It appears that the reaction used in this step*~~ In alternative embodiments, the alkylation process *can be used in other economically very interesting processes* (other than involving 2,6-DMN) butene and p-xylene.

We have determined that the alkylation reaction can be performed with any alkylbenzene and any alkene in the presence of a supported alkali metal catalyst to produce alkylated products. In addition a conjugated diene (such as 1,3-butadiene) can be reacted with an alkylbenzene using the same catalyst in which case the reaction product is an alkenylbenzene.

The tests indicate that, irrespective of whether the starting product is an alkene or a conjugated diene, the precise choice of the catalyst support influences the ratio of branched to straight-chained products in precisely the same manner as we have observed for the reaction between p-xylene and butene.

Alkenylbenzenes can be dehydrocyclised to produce substituted naphthalenes using precisely the same catalysts and reaction conditions as alkylbenzenes.

These tests have led us to the important realisation that 1,3-butadiene can be used as a starting material instead of butene in our process for making 2,6-DMN. In this case the product of the first step in our process will be p-(2-methylbutenyl)-toluene). This compound can be dehydrocyclised to 2,6-DMN under precisely the same conditions as p-(2-methylbutyl)-toluene). ~~*The use of 1,3-butadiene is commercially very interesting and should be protected if possible.*~~

~~*I hope this information can be taken into consideration when drafting the application.*~~

Claims

1. An alkylation process, comprising:

   reacting an alkylbenzene with

   (i) an alkene, or

   (ii) a conjugated diene,

   in the presence of a supported alkali metal catalyst, characterised in that:

   the catalyst is supported on a basic support which desorbs carbon dioxide at a temperature higher than a standard alpha-alumina.

2. An alkylation process acording to claim 1, wherein the basic support desorbs carbon dioxide at a temperature higher than a standard alpha-alumina, according to the procedure for measurement of desorption temperature set out in US-A-1 000 000 and using the standard alpha-alumina precisely described in US-A-1 000 000.

3. An alkylation process according to claim 1 or claim 2 wherein the alkylbenzene is para-xylene.

4. An alkylation process according to any preceding claim wherein the alkene is butene.

5. An alkylation process according to any of claims 1 to 3 wherein the conjugated diene is 1,3-butadiene.

6. An alkylation process according to claim 4, when dependent on claim 3, wherein the process results in the production of p-(2-methylbutyl)-toluene.

7. An alkylation process according to claim 5, when dependent on claim 3, wherein the process results in the production of p-(2-methylbutenyl)-toluene).

8. An alkylation process according to any preceding claim, wherein the alkali metal is sodium, potassium, or a mixture thereof.

9. An alkylation process according to any preceding claim, wherein the basic support comprises powdered sodium or potassium carbonate.

10. A process according to claim 9, when dependent on claim 6 or claim 7, wherein substantially no p-(n-pentyl) toluene or p-(n-pentenyl) toluene respectively is formed.

11. A process for producing a substitited napthalene, comprising:

    (a) producing (i) a modified alkylbenzene
    or (ii) an alkenylbenzene

by reacting (i) an alkene or
(ii) a conjugated diene,
with an alkylbenzene in an alkylation process as defined in any preceding claim;

and

(b) dehydrocyclising the modified alkylbenzene or alkenylbenzene.

12. A process according to claim 11, wherein step (b) is performed in the gas phase using a solid catalyst.

13. A process according to claim 11 or claim 12, wherein step (a) comprises an alkylation process as defined in claim 10 and no separation step is performed between step (a) and step (b).

14. A process according to any of claims 11 to 13, wherein the substituted napthalene is 2,6-dimethylnapthalene.

15. A process for producing polyethylenenapthalate, comprising

(a) producing 2,6-dimethylnapthalene by a process as defined in claim 14,

and

(b) producing polyethylenenapthalate using the 2,6-dimethylnapthalene obtained in step (a).

16. A process for producing a reusable plastic bottle, comprising

(a) producing polyethylenenapthalate by a process as defined in claim 15

and

(b) producing the reusable plastic bottle using the polyethylenenapthalate obtained in step (a).

17. A supported alkali metal catalyst, characterised in that the catalyst is supported on a basic support which desorbs carbon dioxide at a temperature higher than a standard alpha-alumina.

18. A catalyst according to claim 17, wherein the basic support is as defined in claim 2.

19. A catalyst as defined in claim 17 or claim 18, wherein

the basic support is as defined in claim 9.

20. A catalyst as defined in any of claims 17 to 19, wherein the alkali metal is as defined in claim 8.

21. A catalyst as defined in any of claims 17 to 20, which catalyst is suitable for a process as defined in any of claims 1 to 16.

22. A process for producing a catalyst as defined in any of claims 17 to 21, comprising:

    (1) introducing an alkali metal and the basic support into a closed vessel containing an organic solvent under an inert atmosphere, in a weight proportion of 1 part metal to 0.5-500 parts support, and

    (2) stirring the mixture at high speed.

23. A process as defined in claim 22, wherein the organic solvent is an alkene, a conjugated diene, or an alkylbenzene.

24. A process according to any of claims 1 to 10, wherein the reaction temperature is 100 to 200°C.

Note to the Examiner

The characterising feature of claims 1 and 17 might be considered to define the invention in terms of a parameter.

It is submitted that the conditions required for allowability of parameters in a claim, as specified at Guidelines C III-4.7a and T 94/82 are fulfilled; because

(1) this property is the essence of the invention (no alternative really possible without limiting scope) and

(2) parameters can be objectively determined by a test.

It is submitted additionally, (although I accept it is arguable) that the conditions at Guidelines C III - 4.10 are fulfilled, in particular part (ii), such that the whole test does not need to be given in the claim.

D1 also refers to the same test - it may well be the only test commonly used and a skilled person might know to employ it. If not, I have included dependent claims referring to the test to be applied. A skilled person could then go to that document to use the required test.

Divisional applications

It is possible that the synthesis route for 2,6-DMN involving use of para-xylene and butene could be independently patentable, even not using the particular catalyst.

This route involves a reduction of the number of steps over D1, - D1 might cause problems for inventive step, but it could be argued that D1 did not appreciate that para-xylene could be used to produce 2-6-DMN without the requirement for isomerisation.

Note that even if a purification step is needed (because D1's catalyst is used), p-xylene is an alternative starting material and fewer steps are required.

→ possible to file separate application on same day directed