

The present invention relates to a process for the preparation of phenol; it relates more particularly to a process for direct hydroxylation of benzene.

5 Various processes for the syntheses of phenol and more particularly for the synthesis from benzene have been known for a long time (Kirk-Othmer-Thurman C. vol 17, 373-384).

10 Benzene is placed in contact with propylene in the presence of a Lewis acid such as aluminium trichloride or in a heterogeneous medium in the presence of a phosphated silica.

15 The cumene obtained is oxidized in a second step to cumene hydroperoxide which is converted to phenol in a sulphuric medium. This technique is still employed at present, but requires three stages and involves peroxide intermediates which the industry is trying to avoid.

20 For a long time all chemists have attempted to introduce the desired hydroxyl group directly onto the benzene nucleus. For a long time this chemistry has failed. The only publication describing the direct introduction of a hydroxyl group onto a benzene nucleus consists of a paper by Iwamoto published in the Journal of Physical Chemistry, 87, 6, 1983.

25 This benzene hydroxylation reaction is carried out by means of nitrous oxide (N_2O) in the presence of a catalyst based on an oxide of a metal of groups V or VI of the Periodic Classification.

30 Vanadium oxide is the preferred oxide among the oxides of metals of groups V and VI of the Classification. It is preferable to employ this oxide arranged on a support based on silica in a weight quantity of between 1 and 10 % relative to the support. The support preferably consists of silica, since alumina in most cases causes the formation of a mixture of carbon oxides.

35 The said process was of interest but the use of catalysts made it relatively unattractive to industry.

The chemical industry is therefore still looking for a process for the direct hydroxylation of the benzene

nucleus on a simple and readily available substrate.

The present invention has made it possible to reach this objective.

5 Its subject-matter is a process for the preparation of phenol, characterized in that benzene and nitrous oxide are brought into contact on an acidified zeolite.

The zeolite is chosen particularly among the commercial forms, such as:

10 - zeolite ZSM-5 from Mobil-Oil, the preparation of which is described in US Patent 3,702,886,

- zeolite US-Y, sold by Toyo-Soda

- zeolite HY, sold by Union Carbide Chemicals under reference LZY 82, and

15 - zeolite H-mordenite sold by La Grande Paroisse.

It is preferred to employ the commercial zeolite ZSM-5.

The zeolite has an $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio greater than 90, preferably of between 90 and 500.

20 The commercial zeolite is, preferably in the process of the invention, acidified by addition of an inorganic acid chosen from hydrochloric acid, sulphuric acid, nitric acid, perchloric acid and phosphoric acid or of an organic acid chosen from halosulphonic, halomethanesulphonic and halocarboxylic acids and preferably tri-
25 fluoromethanesulphonic acid.

The organic acids offer no advantage when compared with the inorganic acids and present, above all, the disadvantage of being more costly.

30 According to a preferred embodiment, the zeolite is acidified by passing a volume of acid, which has a normality of between 0.1 N and 2 N, of between 10 ml/g and 100 ml/g, per gram of zeolite. This passage may be carried out in a single step or preferably in several successive steps.

35 Nitrous oxide is employed pure or as a mixture with an inert gas which does not contain oxygen, such as nitrogen.

Benzene is preferably introduced as a mixture with nitrous oxide in a molar or volume ratio of nitrous oxide of between 1 and 10, relative to benzene.

5 According to a preferred embodiment, benzene is vaporized, it is mixed with nitrous oxide according to the proportions specified previously and is circulated over the zeolite. The reaction preferably takes place at a temperature of between 300 and 500°C.

10 The reaction gases containing phenol are condensed.

The following examples, given solely by way of indication and without any limitation being implied, make it possible to illustrate the invention.

15 In the examples, the following abbreviations mean:

DC = degree of conversion = product converted/product introduced, in moles

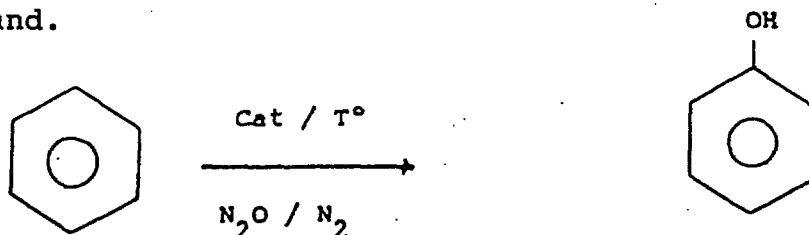
CY = yield on converted product = desired product/converted product, in moles.

20 EXAMPLE 1:

Preparation of the catalyst

25 10 g of commercial zeolite NaZSM5 are placed in contact with 100 ml of a 1N HCl solution at 60°C for 4 hours with stirring. They are allowed to cool and are washed with demineralized water. The solid is filtered off and is dried in the oven at 100°C.

The washing described above is repeated 8 times. The dried product obtained after the 8th washing is ground.



30 EXPERIMENTAL CONDITIONS:

Vapour phase	:	continuous
Catalyst	:	HZSM 5
		pore diam. : 550 ppm

SiO₂/Al₂O₃ ratio = 120

Temperature : test 400°C

Contact time :: 1 second

Molar ratios : benzene/N₂/N₂O

5

2 5 8

1.05 g (2 ml) of HZSM5 catalyst (SiO₂/Al₂O₃ = 120) in powder form, dispersed in 4 g of granular quartz (< 0.8 mm) are introduced into a quartz tubular reactor (length = 16 cm, internal diameter = 1.8 cm).

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A bed of 10 cm of glass beads is then added, allowing the gaseous mixture to be homogenized. The reactor thus packed is conditioned for 15 hours at 350°C under nitrogen in a tubular oven.

15

The reaction is carried out continuously by introducing 1.4 cm³/h of benzene, 1.44 l/h of nitrous oxide and 0.9 l/h of nitrogen.

This gives a molar ratio:

benzene/N₂/N₂O

2 5 8

20

The degree of conversion of benzene is 16 %.

The selectivity for phenol is greater than 95 % (determined: 98 %.)

Control test (a):

25 Example 1 above is reproduced with the exception that the HZSM5 catalyst has an SiO₂/Al₂O₃ ratio of only 50.

The results obtained, all other conditions being unchanged, are the following:

DC = 1.9 %

30

CY > 95 %

EXAMPLE 2:

Example 1 above is reproduced, with the exception that the catalyst is a zeolite HNaZS5 which has an SiO₂/Al₂O₃ ratio of 120.

35

The results obtained, all other conditions being unchanged, are the following:

DC = 9.5 %

CY > 95 %

Control test (b):

Example 1 above is reproduced with the exception that the catalyst is the commercial zeolite NaZSM5 which has an $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 120, untreated.

5 The results obtained, all other conditions remaining unchanged, are the following:

DC = 0

CLAIMS

1. Process for the preparation of phenol, characterized in that benzene and nitrous oxide are brought into contact on an acidified zeolite which has a molar ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$ greater than 90.
5
2. Process according to Claim 1, characterized in that the acidified zeolite is chosen from zeolites HZSM5, HY and H-mordenite which have a molar ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$ of between 90 and 500.
- 10 3. Process according to Claim 1, characterized in that the zeolite is acidified with an inorganic acid.
4. Process according to Claim 1, characterized in that nitrous oxide is employed in a molar ratio of between 1 and 10, calculated relative to benzene.
- 15 5. Process according to Claim 1, characterized in that the reaction is carried out at a temperature of between 300 and 500°C.

