

(19) World Intellectual Property  
Organization  
International Bureau



(43) International Publication Date  
4 August 2005 (04.08.2005)

PCT

(10) International Publication Number  
**WO 2005/071045 A1**

- (51) International Patent Classification<sup>7</sup>: **C10G 47/18**, 47/20, C07C 4/18
- (21) International Application Number: PCT/EP2004/014165
- (22) International Filing Date: 13 December 2004 (13.12.2004)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data: MI2004 A000077 22 January 2004 (22.01.2004) IT
- (71) Applicant (for all designated States except US): **POLIMERI EUROPA S.P.A.** [IT/IT]; Via E. Fermi 4, I-72100 Brindisi (IT).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): **ARCA, Vittorio** [IT/IT]; Via P.E. Venturini 152, I-30015 Chioggia-Venezia (IT). **BOSCOLO BOSCOLETTO, Angelo** [IT/IT]; Viale Veneto 35, I-30019 Sottomarina-Venezia (IT).
- (74) Agents: **DE GREGORI, Antonella** et al.; Ing. Barzano & Zanardo Milano S.p.A., Via Borgonuovo, 10, I-20121 Milan (IT).
- (81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- Published:**
- with international search report
  - before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: PROCESS FOR THE CATALYTIC HYDRODEALKYLATION OF ALKYLAROMATIC HYDROCARBONS

(57) Abstract: Process for the catalytic hydrodealkylation alone of hydrocarbons, comprising C<sub>8</sub>-C<sub>13</sub> alkylaromatic compounds, optionally mixed with C<sub>4</sub>-C<sub>9</sub> aliphatic and cycloaliphatic products, which comprises treating said hydrocarbon compositions, in continuous and in the presence of hydrogen, with a catalyst consisting of a ZSM-5 zeolite, as such or in a bound form, wherein the Si/Al molar ratio in the ZSM-5 ranges from 5 to 35, modified with at least one metal selected from those belonging to groups IIB, VIB, VIII, at a temperature ranging from 400 to 650°C, a pressure ranging from 2 to 4 MPa and a H<sub>2</sub>/charge molar ratio ranging from 3 to 6.



WO 2005/071045 A1

5

PROCESS FOR THE CATALYTIC HYDRODEALKYLATION OF ALKYLAROMATIC HYDROCARBONS

The present invention relates to a process for the catalytic hydrodealkylation of alkylaromatic hydrocarbons.

More specifically, the present invention relates to a process for the catalytic hydrodealkylation of hydrocarbon compositions comprising C<sub>8</sub>-C<sub>13</sub> alkylaromatic compounds, optionally mixed with C<sub>4</sub>-C<sub>9</sub> aliphatic and cycloaliphatic products.

Even more specifically, the present invention relates to a process for the catalytic hydrodealkylation of alkylaromatic hydrocarbons, mixed with aliphatic products, in which concomitant transalkylation, isomerization, disproportioning and condensation reactions are almost quantitatively suppressed. This leads to a high production of benzene, toluene and ethane (BTE), and the reduced or non-formation of methane and condensed products, essentially naphthalene and biphenyl products.

Processes for the catalytic hydrodealkylation of alky-

laromatic hydrocarbons are known in literature. European patent 138,617 describes, for example, a process for converting alkylaromatic hydrocarbons by means of hydrodealkylation which comprises treating a hydrocarbon stream, essentially consisting of ethylbenzene and xylenes, under conventional reaction conditions with a zeolitic catalyst modified with molybdenum. In the process described, however, the general reaction conditions do not allow a hydrodealkylation reaction without there being contemporaneous isomerization, transalkylation, disproportioning and condensation reactions. The limitations towards a selective catalytic hydrodealkylation also emerge from various other processes described in the known art. In some of these, said reaction actually forms a secondary reaction with respect to the isomerization, transalkylation, disproportioning and condensation reactions.

The Applicant has now found that it is possible to effect the catalytic hydrodealkylation alone of C<sub>8</sub>-C<sub>13</sub> alkylaromatic hydrocarbons to benzene, toluene and ethane (BTE) without the concomitant transalkylation, disproportioning, isomerization and condensation reactions which always characterize the processes of the known art, by selecting suitable operating conditions and formulation of a zeolitic catalyst.

In particular, under the operating conditions and with

the composition of the catalyst of the present invention, it has been surprisingly found that the hydrodealkylation reaction is not only quantitatively selective towards the formation of benzene and toluene, but that the benzene/toluene ratio is always distinctly favourable with respect to benzene. The economical advantage of the process can therefore be related to the intrinsic value of both reaction streams: the liquid phase for the remunerative benzene and toluene value, with particular regard to the benzene always produced in higher quantities than toluene; the gaseous phase for the possibility of recycling the ethane produced in any pyrolytic process, for example for recycling to the ovens, with a considerable recovery of energy which this recycling guarantees.

An object of the present invention therefore relates to a process for the catalytic hydrodealkylation process alone of hydrocarbon compositions comprising C<sub>8</sub>-C<sub>13</sub> alkylaromatic compounds, optionally mixed with C<sub>4</sub>-C<sub>9</sub> aliphatic and cycloaliphatic products, which comprises treating said hydrocarbon compositions, in continuous and in the presence of hydrogen, with a catalyst consisting of a ZSM-5 zeolite carrier medium, having an Si/Al molar ratio ranging from 5 to 35, modified with at least one metal selected from those belonging to groups IIB, VIB, VIII, at a temperature ranging from 400 to 650°C, preferably from 450 to

580°C, a pressure ranging from 2 to 4 MPa, preferably from 2.8 to 3.6 MPa, and a H<sub>2</sub>/charge molar ratio ranging from 3 to 6, preferably from 3.8 to 5.2.

According to the present invention, the hydrocarbon charge subjected to hydrodealkylation comprises C<sub>8</sub>-C<sub>13</sub> alkylaromatic compounds, such as ethylbenzene, xylenes, diethylbenzenes, ethylxylenes, trimethylbenzenes, tetramethylbenzenes, propylbenzenes, ethyltoluenes, propyltoluenes, etc. Said charge can derive, for example, from the effluents of reforming units or from units forming pyrolytic processes, such as steam cracking, and optionally contain a mixture of C<sub>4</sub>-C<sub>9</sub> aliphatic and cycloaliphatic products, and organic compounds containing hetero-atoms, such as, for example, sulfur, in the typical quantities generally present in charges coming from reforming units or pyrolytic processes.

The hydrocarbon charge used in the present process can also be subjected to separation treatment, for example distillation or extraction, to concentrate the products to be subjected to subsequent hydrodealkylation, or it can be treated with aromatization processes to increase the concentration of alkylaromatics and reduce the concentration of paraffins. A previous hydrogenation of the charge may also be necessary to eliminate the saturations present in the aliphatic compounds and on the same alkyl substituents

of the aromatic rings. The same hydrogenation can remove sulfur, nitrogen or oxygen from the substances typically present in the charge to be treated, even if this latter aspect is not particularly important as, under the catalytic hydrodealkylation conditions, according to the present invention, these hetero-atoms are quantitatively removed (for example, sulfur as H<sub>2</sub>S).

The hydrodealkylation catalyst, according to the present invention, consists of a ZSM-5 zeolite modified with at least one metal selected from those of groups IIB, VIB and VIII, in particular molybdenum, zinc, nickel, cobalt, palladium, or their mixtures consisting for example of molybdenum/zinc and molybdenum/cobalt, wherein the metals exert a cooperative effect on the hydrodealkylation. Among the metals object of the invention, taken either singly or in pairs, molybdenum is the preferred metal. The composition of the zeolitic carrier medium is particularly important for the embodiment of the present invention which envisages the hydrodealkylation of alkylaromatic compounds in the substantial absence of secondary isomerization, transalkylation, disproportioning and condensation reactions. It has in fact been verified that the use of a ZSM-5 zeolite rich in aluminum, in particular with Si/Al molar ratios ranging from 5 to 35, preferably from 15 to 30, has contributed to obtaining the desired result.

ZSM-5 zeolite is available on the market or can be prepared according to the methods described in U.S. patents 3,702,886 and 4,139,600. The structure of the ZSM-5 zeolite is described by Kokotailo et al. (Nature, Vol. 272, page 5 437, 1978) and by Koningsveld et al. (Acta Cryst. Vol. B43, page 127, 1987 ; Zeolites, Vol. 10, page 235, 1990).

In the process, object of the present invention, it is preferable to use the zeolitic catalyst in a bound form, using a binding substance which gives it shape and consistency, for example mechanical resistance, so that the zeo- 10 lite/binder catalyst is suitable for being conveniently used in an industrial reactor. Examples of binders include aluminas, among which pseudo-bohemite and  $\gamma$ -alumina; clays, among which kaolinite, vermiculite, attapulgite, smectites, 15 montmorillonites; silica; alumino-silicates; titanium and zirconium oxides; combinations of two or more of these, using in such quantities as to give zeolite/binder weight ratios ranging from 100/1 to 1/10.

The dispersion of the metals in the zeolite or zeo- 20 lite/binder catalyst can be carried out according to the conventional techniques, such as impregnation, ion exchange, vapour deposition, or surface adsorption. The incipient impregnation technique is preferably used, with an aqueous or aqueous-organic solution (with the organic sol- 25 vent preferably selected from alcohols, ketones and ni-

triles or their mixtures), containing at least one hydro- and/or organo-soluble compound of the metal, with a total final content of the metal in the catalyst ranging from 0.5 to 10% by weight.

5 The zeolite, with or without binder, is subjected to impregnation with a metal of groups IIB, VIB and VIII. In particular, the catalyst, whether it be bound or not, can be treated according to methods which comprise:

- preparing one or more solutions of metal compounds to  
10 be carried on a medium;
  - impregnating the zeolite with the above solutions;
  - drying the zeolite thus impregnated;
  - calcining the impregnated and dried zeolite, at temperatures ranging from 400 to 650°C;
- 15 optionally repeating the previous steps once or several times according to necessity.

Examples of metal compounds used are: molybdenum(II) acetate, ammonium(VI) molybdate, diammonium(III) dimolybdate, ammonium(VI) heptamolybdate, ammonium(VI)  
20 phosphomolybdate, and analogous sodium and potassium salts, molybdenum(III) bromide, molybdenum(III)-(V) chloride, molybdenum(VI) fluoride, molybdenum(VI) oxychloride, molybdenum(IV)-(VI) sulfide, molybdic acid and the corresponding acid ammonium, sodium and potassium salts, and molybde-  
25 num(II-VI) oxides; cobalt(II) acetate, cobalt(II)

acetylacetonate, cobalt(III) acetylacetonate, cobalt(II) benzoylacetonate, cobalt(II) 2-ethylhexanoate, cobalt(II) chloride, cobalt(II) bromide, cobalt(II) iodide, cobalt(II)-(III) fluoride, cobalt(II) carbonate, cobalt(II) nitrate, cobalt(II) sulfate; nickel(II) acetate, nickel(II) acetylacetonate, nickel(II) bromide, nickel(II) carbonate, nickel(II) nitrate, nickel(II) chloride, nickel(II) iodide, nickel(II) molybdate, nickel(II) sulfate; zinc(II) acetate, zinc(II) acetylacetonate, zinc(II) chloride, zinc(II) bromide, zinc(II) citrate, zinc(II) tartrate, zinc(II) fluoride, zinc(II) iodide, zinc(II) molybdate, zinc(II) nitrate, zinc(II) sulfate, zinc(II) sulfide; palladium(II) acetate, palladium(II) acetylacetonate, palladium(II) bromide, palladium(II) chloride, palladium(II) iodide, palladium(II) nitrate, palladium(II) sulfate, palladium(II) sulfide, palladium(II) trifluoro acetate.

At the end of the impregnation, the total content of metal, single or in pairs, in the catalyst ranges from 0.1 to 10% by weight, preferably from 0.5 to 8% by weight.

At the end of the preparation of the catalyst, this is charged into a fixed bed reactor fed in continuous with the hydrocarbon charge and hydrogen. In this respect, not only is the control of the experimental parameters so far described of absolute importance, but also the selection of the flow-rate of the reagents, in order to obtain a

hydrodealkylation selectivity of the C<sub>8</sub>-C<sub>13</sub> aromatic hydrocarbons optionally mixed with C<sub>4</sub>-C<sub>9</sub> aliphatic and cycloaliphatic hydrocarbons. The feeding flow-rates of the hydrocarbon and hydrogen mixture must be such as to guarantee an LHSV (Liquid Hourly Space Velocity), calculated with respect to the hydrocarbon stream, ranging from 3 to 5 h<sup>-1</sup> and, more preferably, from 3.5 to 4.5 h<sup>-1</sup>. For this purpose, the molar ratio between the hydrogen and charge fed must remain within a range of 3 to 6 mole/mole, more preferably from 3.8 to 5.2 mole/mole.

An experimental apparatus is used, which comprises a fixed bed reactor made of stainless steel with an internal diameter of 20 mm and a total height of 84.5 cm, an electric heating device which surround the reactor, a cooling device, a gas-liquid separator and a high pressure liquid pump.

The isothermal section of the reactor, maintained at a constant temperature by means of automatic control, is charged with the catalyst. The remaining volume of the reactor is filled with an inert solid in granules, for example corundum, to guarantee an optimal distribution and mixing of the gaseous stream of reagents before the catalytic bed and of the heat supplied to the reaction.

A preheater situated before the reactor which operates at a temperature ranging from 200 to 400°C, preferably from

250 to 320°C, also contributes to ensuring an optimum contact of the reagents (charge and hydrogen) in gaseous phase with the catalyst. This system favours the establishment of isothermal conditions in very rapid times, not limited to  
5 the fixed bed alone but along the whole reactor enabling an easier and more accurate control of the operation temperature of the catalyst. The liquid and gaseous effluents produced by the reaction are separated and analyzed by gas chromatography at intervals.

10 The following examples provide a further illustration of the process according to the present invention but should in no way be considered as limiting its scope which is indicated in the enclosed claims.

#### REFERENCE EXAMPLE FOR THE PREPARATION OF THE CATALYSTS

##### 15 Catalyst A (comparative)

Catalyst A is prepared, obtained by mixing a ZSM-5 zeolite and an alumina as binder, the two phases being in a weight ratio of 60/40, and extruding the mixture.

20 The extruded product is calcined in air at 550°C for 5 hours and its BET surface area is 290 m<sup>2</sup>/g.

Once this has reached room temperature, it is crushed and sieved to produce a powder having a dimension ranging from 20 to 40 mesh (from 0.84 mm to 0.42 mm), so that 12.4 g of catalyst powder occupy an equivalent volume of 20 ml.

Catalyst B

Catalyst B is obtained by impregnating catalyst A (50 g) with an aqueous solution (60 ml) containing 1.88 g of ammonium molybdate  $[(\text{NH}_4)_6\text{MO}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}]$  at about 25°C for 16 hours and subsequently put under a nitrogen stream for 12 hours, dried in an oven at 120°C for 4 hours under vacuum and calcined in air at 550°C for 5 hours. The calculated molybdenum content in the catalyst is 2.0% by weight, with respect to the value of 2.1% determined by means of ICP-MS analysis.

Catalyst C

Catalyst C is obtained by impregnating Catalyst A (14 g) with an aqueous solution (17 ml) containing 0.78 g of ammonium molybdate  $[(\text{NH}_4)_6\text{MO}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}]$ , and subsequently following the procedure used for preparing Catalyst B. The calculated molybdenum content is 3.0% weight, in accordance with the value of 3.05% by weight obtained via ICP-MS.

Catalyst D

Catalyst D is obtained by impregnating Catalyst A (50 g) with an aqueous solution (60 ml) containing 3.76 g of ammonium molybdate  $[(\text{NH}_4)_6\text{MO}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}]$ , and subsequently following the procedure used for the preparation of Catalyst A. The calculated molybdenum content is 3.9% weight, in accordance with the value of 4.1% by weight obtained via ICP-MS.

Catalyst E

Catalyst E is obtained by impregnating Catalyst A (50 g) in two steps: a first impregnation with an aqueous solution (60 ml) containing 1.88 g of ammonium molybdate [(NH<sub>4</sub>)<sub>6</sub>MO<sub>7</sub>O<sub>24</sub>•4H<sub>2</sub>O], followed by a second impregnation with an aqueous solution (50 ml) containing 2.77 g of zinc acetate dihydrate [Zn(OCOCH<sub>3</sub>)<sub>2</sub>•2H<sub>2</sub>O]. The impregnation procedure with the first metal is carried out as described for catalyst B, but without calcinations, followed by impregnation with the second metal using the same operating procedure, and final calcination in air at 550°C for 5 hours.

The calculated molybdenum and zinc content in the catalyst is 2.0% by weight and 1.6% by weight, respectively, compared with the values of 2.0% by weight and 1.7% by weight determined by ICP-MS.

Catalyst F

Catalyst F is obtained by impregnating Catalyst A (20 g) in two steps: a first impregnation with an aqueous solution (24 ml) containing 1.15 g of ammonium molybdate [(NH<sub>4</sub>)<sub>6</sub>MO<sub>7</sub>O<sub>24</sub>•4H<sub>2</sub>O], followed by a second impregnation with an aqueous solution (23 ml) containing 0.5 g of cobalt nitrate hexahydrate [Co(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O]. The impregnation procedure with the two metals is carried out as described for catalyst E.

The calculated molybdenum and cobalt content in the

catalyst is 3.0% by weight and 0.5% by weight, respectively, compared with the values of 3.0% by weight and 0.5% by weight determined by ICP-MS.

#### Catalyst G

5 Catalyst G is obtained by impregnating Catalyst A (50 g) with an aqueous solution (50.5 ml) containing 1.85 g of nickel nitrate  $[\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ , following the procedure used for preparing Catalyst B.

The calculated nickel content is 0.74% weight with respect to the value of 0.77% by weight obtained via ICP-MS.

#### Catalyst H

Catalyst H is obtained by impregnating Catalyst A (50 g) with an aqueous solution (60 ml) containing 4.0 g of nickel nitrate  $[\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ , following the procedure used for preparing Catalyst B.

The calculated nickel content is 1.6% weight with respect to the value of 1.7% by weight obtained via ICP-MS.

#### Catalyst I

Catalyst I is obtained by impregnating Catalyst A (14 g) with an aqueous solution of 0.6 g of palladium acetate  $[\text{Pd}(\text{OCOCH}_3)_2]$  in 20 ml of acetone, following the procedure used for preparing Catalyst B.

The calculated palladium content is 2.0% weight compared with the value of 2.1% by weight obtained via ICP-MS.

25 Examples 1-4 (Comparative)

The reactor is charged with 20 cm<sup>3</sup> (12.4 g) of catalyst A, whereas the remaining volume is filled with corundum in granules to guarantee an optimum distribution and mixing of the gaseous stream of reagents and of the heat  
5 supplied to the reaction.

Two different charges, whose composition is indicated in Table 1 below, suitably mixed with hydrogen and pre-heated to 280°C, are fed, alternately, to the reactor. In both charges, the aliphatic part is carried by the C<sub>4</sub>-C<sub>9</sub>  
10 products and by the saturated C<sub>5</sub> indane ring.

Table 1 - Composition of the feeding charge

	Charge 1 weight %	Charge 2 weight %
Ethylbenzene	43	34
o, m, p - xylene	20	32
indane	12	9
cumene	1	1
n-propylbenzene	3	3
2-, 3-, 4- ethyltoluene	16	16
Σ ( C <sub>4</sub> - C <sub>9</sub> Aliphatic. + C <sub>9+</sub> Arom. )	5	5
Total	100	100

The reaction is carried out at a pressure of 3 MPa with a reagent charge flow rate so as to have an LHSV of 3.9-4.1 h<sup>-1</sup>, and a molar ratio H<sub>2</sub>/charge of 4.2-4.4. The re-  
25 sults are shown in Table 2 below.

Table 2

	Ex. 1	Ex. 2	Ex. 3	Ex. 4
Catalyst	A	A	A	A
Metal	---	---	---	---
Reaction temperature	450°C	510°C	510°C	550°C
Charge	Charge 1	Charge 1	Charge 2	Charge 2
Charge conversion (%)	80.0	80.2	78.6	81.3
Liquid effluent composition	weight %	weight %	weight %	weight %
Methane	3.2	6.9	10.3	13.8
$\Sigma C_2$	7.0	10.8	11.2	11.4
$\Sigma C_3$	7.9	3.0	3.1	1.3
$\Sigma C_4 - C_5$	0.1	0.1	--	--
Ethylbenzene	2.6	1.5	0.9	0.8
o, m, p- xylene	15.1	14.8	15.9	14.5
indane	--	--	--	--
cumene	---	---	---	---
$\Sigma C_9 - C_{9+}$ aromatic	6.9	5.6	5.5	5.0
Benzene	27.4	26.6	24.0	26.3
Toluene	29.6	31.1	28.4	26.9
Total	100.0	100.0	100.0	100.0
$\Sigma$ (Bz + Tol)	57.0	57.7	52.4	53.3
Selectivity to (Bz + Tol) (w %)	71.3	71.9	66.7	65.6
R (Bz + Tol)	0.93	0.86	0.76	0.98

Examples 5 - 20

The same procedure is used as in the previous examples 1-4, with the substantial difference that catalyst A is substituted by catalysts B-I described above. The results are indicated in the enclosed tables 3, 4 and 5.

Table 3

	Ex. 1	Ex. 5	Ex. 6	Ex. 7	Ex. 8	Ex. 9
Catalyst	A	B	D	G	H	I
Metals	---	Mo 2% w	Mo 4% w	Ni 0.8% w	Ni 1.7% w	Pd 2% w
Reaction temperature	450°C	450°C	450°C	450°C	450°C	450°C
Charge	Charge 1	Charge 1	Charge 1	Charge 1	Charge 1	Charge 2
Charge conversion (%)	80.0	81.8	80.7	81.2	83.2	81.4
Liquid effluent composition	weight %	weight %	weight %	weight %	weight %	weight %
Methane	3.2	0.6	0.4	1.7	1.7	0.4
$\Sigma C_2$	7.0	19.0	18.0	11.4	14.5	18.0
$\Sigma C_3$	7.9	2.7	2.1	5.9	5.5	3.1
$\Sigma C_4 - C_5$	0.1	0.1	--	0.1	0.1	0.1
Ethylbenzene	2.6	0.7	0.5	2.3	1.1	0.2
o, m, p- xylene	15.1	15.9	14.6	14.3	13.7	15.6
indane	--	--	--	--	--	--
cumene	--	--	--	--	--	--
$\Sigma C_9 - C_{9+}$ aromatic	6.9	3.2	4.3	5.7	4.4	3.8
Benzene	27.4	37.1	37.5	30.6	31.5	29.5
Toluene	29.6	20.7	22.6	28.0	27.5	29.3
Total	100.0	100.0	100.0	100.0	100.0	100.0
$\Sigma$ (Bz + Tol)	57.0	57.8	60.1	58.6	59.0	58.8
Selectivity to (Bz + Tol) (w %)	71.3	70.7	74.5	72.2	70.9	72.2
R (Bz + Tol)	0.93	1.79	1.66	1.09	1.15	1.01

Table 4

	Ex. 10	Ex. 11	Ex. 12	Ex. 13	Ex. 14	Ex. 15	Ex. 16	Ex. 17	Ex. 18
Catalyst	B	B	B	C	C	G	H	I	I
Metals	Mo 2% w 510 °C	Mo 2% w 510 °C	Mo 2% w 550 °C	Mo 3% w 510 °C	Mo 3% w 550 °C	Ni 0.8% w 510 °C	Ni 1.7%w 510 °C	Pd 2%w 510 °C	Pd 2%w 525 °C
Reaction temperature	510 °C	510 °C	550 °C	510 °C	550 °C	510 °C	510 °C	510 °C	525 °C
Charge	Charge 1	Charge 2	Charge 2	Charge 2	Charge 2	Charge 1	Charge 1	Charge 2	Charge 2
Charge conversion (%)	85.8	84.5	88.7	86.0	86.5	83.6	85.2	86.2	87.0
Liquid effluent composition	weight %	weight %	weight %	weight %	weight %	weight %	weight %	weight %	weight %
Methane	1.3	3.2	7.0	1.0	3.5	3.5	5.8	2.8	2.9
$\Sigma C_2$	17.3	20.6	19.2	18.1	17.7	12.3	14.1	16.5	16.8
$\Sigma C_3$	2.0	3.8	2.2	1.4	1.4	5.0	2.6	1.9	0.9
$\Sigma C_4 - C_5$	0.1	0.1	0.1	---	---	0.1	---	---	---
Ethylbenzene	0.3	0.2	0.1	0.1	0.5	0.2	0.1	0.1	0.1
o, m, p- xylene	10.4	13.1	10.0	9.9	12.4	13.7	12.4	11.4	10.9
indane	--	--	--	--	--	--	--	--	--
cumene	--	--	--	--	--	--	--	--	--
$\Sigma C_9 - C_{9+}$ aromatic	3.9	3.0	1.9	4.0	1.8	4.6	3.0	3.1	4.0
Benzene	35.4	27.2	29.6	36.0	29.9	32.8	30.3	32.9	34.4
Toluene	29.3	28.8	29.9	29.5	32.8	27.4	30.8	31.3	30.0
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
$\Sigma$ (Bz + Tol)	64.7	56.0	59.5	65.5	62.7	60.2	61.1	64.2	64.4
Selectivity (Bz + Tol) (w%)	75.4	66.3	67.1	76.2	72.5	72.0	71.7	74.5	74.0
R (Bz + Tol)	1.21	0.94	0.99	1.22	0.91	1.20	0.98	1.05	1.15

Table 5

	Ex. 19	Ex. 20
Catalyst	E	F
Metals	Zn 1.7 % w + Mo 2 % w	Co 0.5 % w + Mo 3 % w
Reaction temperature	510°C	450°C
Charge	Charge 2	Charge 2
Charge conversion (%)	84.3	80.3
Liquid effluent composition	weight %	weight %
Methane	3.8	1.0
$\Sigma C_2$	16.5	19.7
$\Sigma C_3$	5.7	2.8
$\Sigma C_4 - C_5$	0.1	0.1
Ethylbenzene	0.8	0.3
o, m, p- xylene	13.1	17.0
indane	--	--
cumene	--	--
$\Sigma C_9 - C_{9+}$ aromatic	3.3	3.6
Benzene	29.6	32.6
Toluene	27.1	22.9
Total	100.0	100.0
$\Sigma$ (Bz + Tol)	56.7	55.5
Selectivity to (Bz + Tol) (w %)	67.3	69.1
R (Bz + Tol)	1.09	1.42

The hydrodealkylation reaction carried out at a temperature of 450°C with Charge 1 (see Table 3) shows how the presence of one of the metals and ZSM-5, according to the invention, distinctly favours the selective dealkylation of the aromatics, by inhibiting the by-production of methane to favour the net increase in ethane, with respect to the reaction carried out with the catalyst as such (Example 1). Furthermore, not only is the

production of benzene and toluene increased, but their weight ratio (benzene/toluene) becomes unexpectedly and distinctly favourable towards benzene (Examples 5-8). In the case of the reaction carried out on Charge 2 (Example 5 9), in addition to the positive results already indicated for Charge 1, it is observed that even with a greater quantity of xylenes (about 1.5 times by weight with respect to Charge 1), their concentration in the effluent does not increase, maintaining the typical value of that relating to 10 the effluent deriving from the reaction carried out on Charge 1. This further evidence indicates the capacity of the process, object of the invention, of guaranteeing, also in the case of a "heavier" charge, by an increase in the content of xylenes, a selective dealkylation without 15 concomitant isomerization, transalkylation, disproportioning and condensation reactions.

At temperatures higher than 450°C (Table 4) and always in the presence of the catalyst impregnated with metal, further significant increases in the conversion of the 20 charges (1 and 2) and selectivity to benzene plus toluene, are contemporaneously obtained, with a ratio between the benzene and toluene produced which is still favourable towards benzene. The increased selectivity observed with respect to the products obtained in the liquid phase, is 25 also observed in the gaseous phase, where an increase in

the production of ethane is registered, whereas the increase in the concentration of methane is directly connected to the further reduction in the content of xylenes and C<sub>9</sub>-C<sub>9+</sub> aromatics which are selectively  
5 dealkylated (Examples 10-18).

This result is particularly important as the amount of xylenes and higher aromatics converted per single passage by the process object of the invention is such as to sustain the recycling of what remains in the effluent.

10 The hydrodealkylation reaction carried out with a catalyst impregnated with pairs of metals, at both 450°C and 510°C, (Examples 19-20, Table 5) further improves, with respect to the single metal, the benzene/toluene ratio, i.e. it makes the reaction towards benzene, total  
15 dealkylation product, even more selective.

Examples 2 bis, 5 bis, 10 bis

Table 6 indicates the examples relating to hydrodealkylation reactions carried out in the previous examples with the substantial difference that sulfur is  
20 added to Charge 1 in the form of dimethyl disulfide (DMDS).

Table 6

	Ex. 2	Ex. 2 bis	Ex. 5	Ex. 5 bis	Ex. 10	Ex. 10 bis
Catalyst	A	A	B	B	B	B
Metals	---	---	Mo 2% w	Mo 2% w	Mo 2% w	Mo 2% w
Reaction temperature	510°C	510°C	450°C	450°C	510°C	510°C
Charge	Charge 1	Charge 1	Charge 1	Charge 1	Charge 1	Charge 1
Presence of DMDS (ppm/w)*	-	200	-	200	-	200
Charge conversion (%)	80.2	82.8	81.8	82.0	85.8	85.1
Benzene	26.6	24.7	37.1	36.0	35.4	33.7
Toluene	31.1	29.8	20.7	21.4	29.3	30.3
$\Sigma$ (Bz + Tol)	57.7	54.5	57.8	57.4	64.7	64.0
Selectivity to (Bz + Tol) (w %)	71.9	65.8	70.7	70.0	75.4	75.2
R (Bz + Tol)	0.86	0.83	1.79	1.68	1.21	1.11

\* equal to 136 ppm/w as sulfur equivalent

Under the process conditions, object of the invention, the charge is quantitatively hydro-desulfurated as the corresponding H<sub>2</sub>S remains lower than 0.5 ppm/w in the liquid effluent.

5           The examples of Table 6 demonstrate that the hydrodealkylation reaction proceeds without any alternation in the catalytic activity when the catalyst is impregnated with the metal. In particular, it is evident that already at 450°C, the results obtained of yield to benzene plus  
10 toluene and the benzene/toluene ratio are distinctly higher than those obtained at 510°C with the non-treated catalyst, whereas the conversions of the charge at the two temperatures are identical.

15

20

25

CLAIMS

1. A process for the catalytic hydrodealkylation alone of hydrocarbons comprising C<sub>8</sub>-C<sub>13</sub> alkylaromatic compounds, optionally mixed with C<sub>4</sub>-C<sub>9</sub> aliphatic and cycloaliphatic products, which comprises treating said hydrocarbon compositions, in continuous and in the presence of hydrogen, with a catalyst consisting of a ZSM-5 zeolite, having an Si/Al molar ratio ranging from 5 to 35, modified with at least one metal selected from those belonging to groups IIB, VIB, VIII, at a temperature ranging from 400 to 650°C, a pressure ranging from 2 to 4 MPa and an H<sub>2</sub>/charge molar ratio ranging from 3 to 6.
2. The process according to claim 1, wherein the hydrodealkylation reaction takes place at temperatures ranging from 450 to 580°C, pressures ranging from 2.8 to 3.6 MPa, H<sub>2</sub>/charge molar ratios ranging from 3.8 to 5.2, and with flow-rates of the reagents which are such as to guarantee an LHSV (Liquid Hourly Space Velocity), calculated with respect to the hydrocarbon stream, ranging from 3 to 5 h<sup>-1</sup>, preferably 3.5 to 4.5 h<sup>-1</sup>.
3. The process according to claims 1 and 2, wherein the hydrocarbon charge subjected to hydrodealkylation comprises C<sub>8</sub>-C<sub>13</sub> alkylaromatic compounds selected from ethylbenzene, xylenes, propylbenzenes, ethyltoluenes, trimethylbenzenes, diethylbenzenes, ethylxylenes, tetramethylbenzenes,

propyltoluenes, ethyltrimethylbenzenes, triethylbenzenes, dipropyltoluenes.

4. The process according to claim 3, wherein the C<sub>8</sub>-C<sub>13</sub> alkylaromatic hydrocarbon charge comes from reforming units  
5 or from units effecting pyrolytic processes, or from steam cracking.

5. The process according to claims 1-4, wherein the hydrocarbon charge subjected to hydrodealkylation comprises C<sub>8</sub>-C<sub>13</sub> alkylaromatic compounds, optionally mixed with C<sub>4</sub>-C<sub>9</sub>  
10 aliphatic and cycloaliphatic products and organic compounds containing hetero-atoms.

6. The process according to claims 1-5, wherein the catalyst consists of a ZSM-5 zeolite in bound form, with binders selected from aluminas, among which pseudo-bohemite and  
15  $\gamma$ -alumina; clays, among which kaolinite, smectites, montmorillonites; silica; alumino-silicates; titanium and zirconium oxides; their mixtures with zeolite/binder weight ratios ranging from 100/1 to 1/10.

7. The process according to claims 1-6, wherein the ZSM-5  
20 catalyst/binder is modified with at least one metal selected from those belonging to groups IIB, VIB and VIII.

8. The process according to any of the previous claims, wherein the metal belonging to groups IIB, VIB and VIII, is selected from molybdenum, zinc, nickel, cobalt, palladium,  
25 and their mixtures.

9. The process according to claim 8, wherein the metal is molybdenum.

10. The process according to any of the previous claims, wherein the ZSM-5 zeolite is characterized by an Si/Al molar ratio ranging from 15 to 30.

11. The process according to any of the previous claims, wherein the dispersion of metals on the catalyst can be carried out according to techniques selected from impregnation, ion exchange, vapour deposition or surface adsorption.

12. The process according to any of the previous claims, wherein the ZSM-5 zeolite as such or in bound form is impregnated with metals of groups IIB, VIB and VIII according to methods which comprise:

- 15 - preparing one or more solutions of metal compounds to be carried on a medium;
- impregnating the zeolite with the above solutions;
- drying the zeolite thus impregnated;
- calcining the impregnated and dried zeolite, at temperatures ranging from 400 to 650°C;
- 20 - optionally repeating the previous steps once or several times.

13. The process according to claim 12, wherein the dispersion of metals on the catalyst takes place by impregnation with an aqueous or aqueous-organic solution, with the or-

25

ganic solvent selected from alcohols, ketones and nitriles or their mixtures, containing at least one hydro- or organo-soluble compound of the metal in such concentrations that the total final content of the metal in the catalyst  
5 ranges from 0.1 to 10% by weight.

14. The process according to any of the previous claims, wherein the total content of the metal in the catalyst ranges from 0.5 to 8% by weight.

INTERNATIONAL SEARCH REPORT

International Application No  
PCT/EP2004/014165

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 C10G47/18 C10G47/20 C07C4/18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 C10G C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 138 617 A (STANDARD OIL CO) 24 April 1985 (1985-04-24) cited in the application page 2, last paragraph; claims 1,6,10,12; example 1 page 4, paragraph 1 page 5, paragraph 1 page 8, paragraph 4	1-14
X	US 5 689 027 A (OLSON DAVID H ET AL) 18 November 1997 (1997-11-18) column 4, last paragraph; claims 1-4,9,10,20 column 8, last paragraph	1-14
A	EP 0 109 962 A (TORAY INDUSTRIES) 13 June 1984 (1984-06-13) claims 1-12; examples 1-3	1

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

° Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

10 June 2005

Date of mailing of the international search report

17/06/2005

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Gilliquet, J-N

INTERNATIONAL SEARCH REPORT

International Application No  
PCT/EP2004/014165

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 877 374 A (NACAMULI GERALD J ET AL) 2 March 1999 (1999-03-02) column 13, paragraph 2-4; claims 1,5; examples 1-6; table 1 -----	1
A	US 4 351 979 A (CHU YUNG F ET AL) 28 September 1982 (1982-09-28) claims 1,3,9,12; example 1; table 1 -----	1

## INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP2004/014165

Patent document cited in search report		Publication date	Patent family member(s)	Publication date			
EP 0138617	A	24-04-1985	AT 40348 T	15-02-1989			
			BR 8405224 A	27-08-1985			
			CA 1227809 A1	06-10-1987			
			CN 85101896 A ,B	17-01-1987			
			DE 3476379 D1	02-03-1989			
			EP 0138617 A2	24-04-1985			
			JP 1860842 C	27-07-1994			
			JP 5076453 B	22-10-1993			
			JP 60105636 A	11-06-1985			
			US 5689027	A	18-11-1997	US 5516956 A	14-05-1996
US 5625104 A	29-04-1997						
CA 2203365 A1	30-05-1996						
DE 69520592 D1	10-05-2001						
DE 69520592 T2	12-07-2001						
EP 0792251 A1	03-09-1997						
ES 2155538 T3	16-05-2001						
JP 10509720 T	22-09-1998						
WO 9616005 A1	30-05-1996						
US 5705726 A	06-01-1998						
US 5849968 A	15-12-1998						
EP 0109962	A	13-06-1984				EP 0109962 A1	13-06-1984
						DE 3272042 D1	21-08-1986
US 5877374	A	02-03-1999	AU 6771298 A	22-10-1998			
			CA 2283724 A1	08-10-1998			
			DE 69803531 D1	14-03-2002			
			DE 69803531 T2	19-09-2002			
			EP 0909266 A1	21-04-1999			
			TW 412518 B	21-11-2000			
			WO 9843932 A1	08-10-1998			
US 4351979	A	28-09-1982	US 4283584 A	11-08-1981			