

(11) (21) (C) **2,103,116**
(22) 1993/11/15
(43) 1995/05/16
(45) 2000/03/07

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(51) Int.Cl.⁵ C07C 15/08, C07C 2/86

- (54) **PRODUCTION DE PARA-XYLENE PAR METHYLATION
SELECTIVE DU TOLUENE AU MOYEN D'HALOGENURES
DE METHYLE**
(54) **PRODUCTION OF PARA-XYLENE BY SELECTIVE
METHYLATION OF TOLUENE WITH METHYL HALIDES**

(57) The selective methylation of toluene to produce para-xylene is effected by reacting toluene with a methyl halide at a temperature ranging from about 100 to about 500°C and a pressure ranging from about 1 to about 10 atmospheres, in the presence of a shape-selective zeolite catalyst in protonated form having a Si/Al ratio of at least about 25, the zeolite catalyst being either unmodified or modified with a heteropoly acid.

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ABSTRACT

The selective methylation of toluene to produce para-xylene is effected by reacting toluene with a methyl halide at a temperature ranging from about 100 to about 500°C and a pressure ranging from about 1 to about 10 atmospheres, in the presence of a shape-selective zeolite catalyst in protonated form having a Si/Al ratio of at least about 25, the zeolite catalyst being either unmodified or modified with a heteropoly acid.

The present invention relates to an improved process for the production of para-xylene. More particularly, the invention is directed to a process for the selective methylation of toluene to produce
5 para-xylene.

para-Xylene is an industrial feedstock whose demand stems mainly from its use in the production of dimethyl terephthalate (DMT) and purified terephthalic acid (PTA). DMT and PTA, in turn, are used in the
10 production of polyester fibers and films, polyethylene terephthalate and polybutene terephthalate. para-Xylene is also used in the production of herbicides and oil additives.

para-Xylene is generally produced by
15 reforming of naphtha to obtain xylenes-rich stream followed by separation from three close boiling C₈ aromatics, namely, meta-xylene, ortho-xylene and ethylbenzene. The meta- and ortho-xylenes are isomerized to obtain an equilibrium mixture of ortho-,
20 meta- and para-xylenes and then recycled for para-xylene separation. Since the equilibrium mixture of the three xylenes contains only about 24% of para-xylene, separation and isomerization steps are repeated several times, thereby increasing the cost of para-xylene
25 production to a relatively high level.

Another principal process for the production of xylenes is referred to as toluene disproportionation. For example, in the selective
30 disproportionation process developed by the Mobil Chemical Company, a toluene feed and a hydrogen-rich recycle gas are reacted at elevated temperatures (>450°C) over a catalyst to produce benzene and mixed

xylenes containing about 90 wt.% para-xylene. About 30 wt.% toluene is converted per pass; the unconverted toluene is separated downstream and recycled.

5 para-Xylene can also be produced using xylenes as feedstock. The process involves isomerization and separation of xylenes. Toluene is a preferred feedstock compared to xylenes due to its lower cost and wider availability.

10 The current para-xylene processes which use toluene as feedstock, such as Mobil's selective disproportionation process, suffer from major disadvantages as these processes require expensive hydrogen-rich gas, high temperatures and pressures. Processes requiring hydrogen are not only economically
15 less attractive but also hazardous due to high pressure hydrogen.

As an alternative, methylation of toluene is an attractive and direct method of producing para-xylene. However, the development of a suitable
20 alkylating agent and a selective catalyst is critical to successfully implementing such a process scheme. A number of studies on the methylation of toluene using methanol as an alkylating agent over a ZSM-5 type zeolite catalyst have been reported, for example, by
25 W. W. Kaeding et al. in the Journal of Catalysis, Vol. 67, p. 159-174 (1981) and by L. B. Young et al. in the Journal of Catalysis, Vol. 76, p. 418-432 (1982). Although para-xylene is produced in good yield, the use of methanol as an alkylating agent is not economically
30 very attractive. This is mainly because the production of methanol from coal or natural gas is a multistep process which is both energy and cost intensive, as it

requires conversion of the coal or natural gas to synthesis gas by high temperature steam reforming, purification of the synthesis gas and fortification thereof with additional hydrogen, and catalytic
5 conversion of the synthesis gas to methanol at a temperature of about 300°C and high pressures, ranging from 200 to 350 atm. On the other hand, if a para-xylene selectivity higher than 90% is desired, the alkylation reaction must be carried out at high
10 temperatures (>550°C). A further drawback to utilizing methanol as an alkylating agent stems from the water which is produced as a by-product during the alkylation and which deactivates the catalyst.

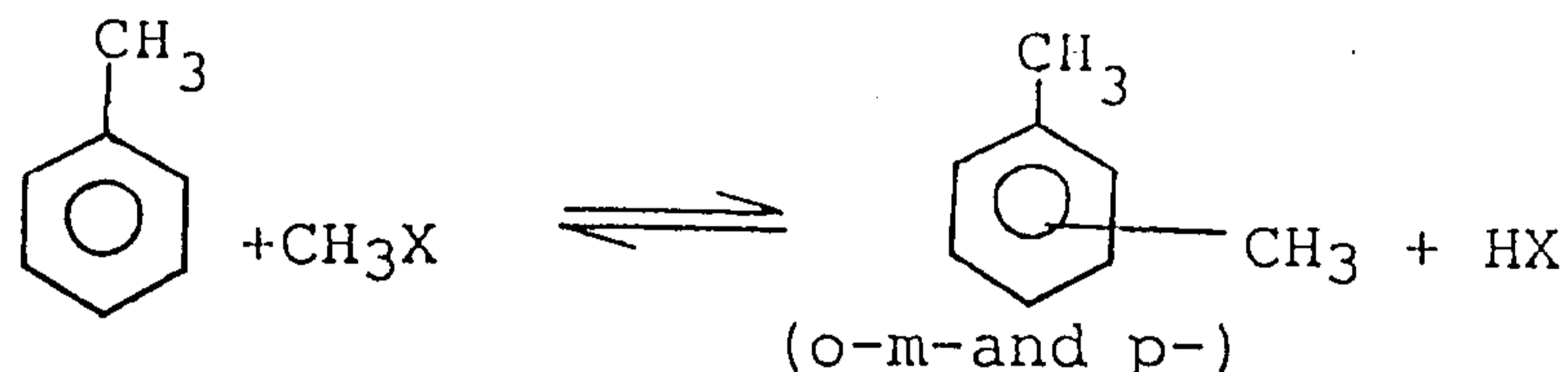
It is therefore an object of the present
15 invention to overcome the above drawbacks and to provide a process for the production of para-xylene with high selectivity, at less severe conditions of temperature and pressure than those encountered in the prior art.

20 In accordance with the invention, there is thus provided a process for the selective methylation of toluene to produce para-xylene, which comprises reacting toluene with a methyl halide at a temperature ranging from about 100 to about 500°C and a pressure
25 ranging from about 1 to about 10 atmospheres, in the presence of a shape-selective zeolite catalyst in protonated form having a Si/Al ratio of at least about 25, the zeolite catalyst being either unmodified or modified with a heteropoly acid.

30 The expression "unmodified, shape-selective zeolite catalyst" as used herein refers to a shape-selective zeolite catalyst whose active sites have not

been modified or altered by reaction of the catalyst with another substance.

The methylation of toluene with methyl halide generally yields a mixture of xylenes, according to the following equation:



wherein X is a halogen atom. As the thermodynamic equilibrium concentrations of ortho-, meta- and para-xylenes are in ratio of 1 : 2 : 1, Applicants have found quite unexpectedly that the more useful para-xylene can be selectively produced at temperatures less than 500°C by using a shape selective aluminosilicate catalyst such as a ZSM-5 type zeolite, provided that such a zeolite catalyst be in protonated form and have a Si/Al ratio of at least about 25, and that it be unmodified or modified with a heteropoly acid. The shape selective behaviour of ZSM-5 zeolite is attributed to its unique three dimensional network of elliptical straight channels and near circular zigzag channels. Since the critical diameter of para-xylene molecules is smaller than ortho- or meta-xylene molecules, para-xylene diffuses much faster than ortho or meta-xylene inside the protonated ZSM-5 zeolite channels. Consequently, the equilibrium mixture of xylenes inside the zeolite channels gets depleted in para-xylene, as more and more para-xylene diffuses out of the channels. As most of the acid sites are located inside the zeolite channels, the ortho- and meta-xylenes quickly undergo isomerization to produce para-

5 xylene in order to maintain the equilibrium concentration. The reverse reaction, that is, the isomerization of para-xylene to produce undesirable ortho- and meta-xylenes, occurs to a very small extent due to the limited active sites on the external surface of the zeolite crystals. This leads to a product mixture rich in para-xylene.

10 Protonation of the zeolite catalyst activates the catalyst for the selective alkylation of toluene with the methyl halide. Preferably, from about 10 to about 100% of the Na⁺ ions contained in the zeolite catalyst are replaced with H⁺ ions. The degree of H⁺ exchange, i.e.

$$\frac{[H^+]}{[H^+] + [Na^+]} \times 100,$$

15 determines the number of protons associated with the aluminum atoms in the zeolite. Protonation can be carried out by impregnating the catalyst with an aqueous solution of HCl or other mineral acid, or with an aqueous solution of NH₄NO₃, followed by calcination at temperatures of 400-500°C for a period of about 4 hours. The ZSM-5 zeolite, on the other hand, can be prepared by the method described in US Patent N° 3,702,886.

25 When use is made of an unmodified, protonated zeolite catalyst, the catalyst used preferably has a Si/Al ratio of about 50.

30 According to a preferred embodiment of the invention, where use is made of a protonated zeolite catalyst having a Si/Al ratio less than about 50, such a catalyst is modified by treatment with a heteropoly

acid. Examples of suitable heteropoly acids which may be used for modifying the catalyst include 12-tungstophosphoric acid ($H_3PW_{12}O_{40}$), 12-tungstosilicic acid ($H_4SiW_{12}O_{40}$) and 12-molybdophosphoric acid ($H_3PMO_{12}O_{40}$). These acids have a high thermal stability, high solubility in water and high Brönsted acidity. Treatment is effected by impregnating the catalyst with an aqueous solution of the heteropoly acid and thereafter evaporating the water. The heteropoly acid deposited on the catalyst remains solid at the operating temperatures, i.e. up to 500°C. Preferably, the modified zeolite catalyst comprises from about 0.5 to about 25 wt.% of heteropoly acid.

Modification of the protonated zeolite catalyst with a heteropoly acid has been found to increase the para-xylene selectivity in the case where the catalyst used has a Si/Al ratio less than about 50. It is believed that the increased selectivity for para-xylene is due to the heteropoly acid blocking the active sites on the outer surface of the catalyst which are responsible for side reactions leading to the formation of trimethylbenzenes and higher aromatic hydrocarbons.

The methyl halide which is used as alkylating agent can be methyl chloride, methyl bromide or methyl iodide. Where use is made of methyl chloride, such an alkylating agent is preferably produced by chlorination of methane or natural gas. Commercial scale production of methyl chloride is usually carried out by thermal chlorination of methane, also called oxyhydrochlorination, at temperatures of 300-450°C. The reaction is highly selective to methyl chloride. For

example, using a silica-supported CuCl-KCl-LaCl_3 catalyst at 340°C , and a reactant mixture of 40% CH_4 , 40% HCl and 20% O_2 , methyl chloride selectivity in the range of 60-85% at methane conversion in the range of 18-43% has been reported by C.E. Taylor et al in "Methane Conversion", Studies in Surface Science Catalysis, Vol 36, pages 483-489 (1988). The chlorination of methane can also be carried out by photochemical methods, wherein a mixture of methane and chloride is exposed to an ultraviolet radiation with a wavelength in the region 250 to 500 nm at low temperature.

The methylation of toluene with the methyl halide over the protonated zeolite catalyst is preferably carried out at a temperature of about 300 to about 400°C , with a weight hourly space velocity of the reactants ranging from about 0.01 to about 10 h^{-1} , preferably from about 0.1 to about 1 h^{-1} . The toluene/methyl halide ratio generally ranges from about 0.1 to about 10.

Where use is made of natural gas-derived methyl chloride, the invention provides an economical route for producing para-xylene with high selectivity, while utilizing abundantly available natural gas resources.

Further features and advantages of the invention will become more readily apparent from the following description of a preferred embodiment as illustrated by way of example in the accompanying drawings, in which:

Figure 1 is a flow diagram of a process for producing para-xylene according to the invention.

In the process which is schematically illustrated in Fig. 1, para-xylene is produced by the selective methylation of toluene with natural gas-derived methyl chloride. Oxyhydrochlorination of natural gas is carried out in a first stage reactor 10 to produce methyl chloride which is used for selectively methylating toluene in a second stage reactor 12. Natural gas, hydrogen chloride and air are fed via feed lines 14, 16 and 18, respectively, to reactor 10 containing a fixed bed of silica-supported CuCl-KCl-LaCl₃ catalyst maintained at about 350°C. The product of reaction which is discharged via line 20 and comprises a mixture of methyl chloride, other chloromethanes, unreacted hydrogen chloride and water is passed through a heat exchanger 22 for lowering the temperature from about 350°C to about 20°C, and then sent to a separator 24 for separating the methyl chloride from the unreacted hydrogen chloride, air and the water which are discharged as by-products via line 26. The hydrogen chloride discharged via line 26 can be recycled as a feedstock to the reactor 10. The separated methyl chloride is sent via line 28 to the reactor 12 where it is reacted with toluene fed through line 30. The reactor 12 contains a fixed bed of protonated ZSM-5 zeolite catalyst maintained at a temperature of about 375°C. The product of reaction which is discharged via line 32 and comprises a mixture of C₂-C₄ hydrocarbons, aromatics, hydrogen chloride and unreacted toluene is passed through a heat exchanger 34 for lowering the temperature from about 375°C to about 20°C, and then sent to a stripper column 36. The C₂-C₄ hydrocarbons are stripped off in the stripper 36 and

discharged via line 38 for storage or consumption as gaseous fuel. The hydrogen chloride which is recovered as a by-product is recycled via line 40 to the first stage reactor 10. The remaining aromatics which are removed at the bottom of the stripper column 36 are sent via line 42 to a distillation column 44 for recovery of the unreacted toluene and separation of the C₈ aromatics. The lighter toluene fraction is recycled via line 46 to the second stage reactor 12. Benzene obtained as a by-product is discharged via line 48. The heavier xylene fraction containing small quantities of ethylbenzene and C₉ aromatics is removed at the bottom of the distillation column 44 and sent via line 50 to a mixed xylenes separation unit (not shown) for the extraction of para-xylene.

The following non-limiting examples further illustrate the invention.

EXAMPLE 1

Methylation of toluene with methyl chloride was carried out using a fixed bed continuous flow reactor. The reactor was charged with 0.2 g of ZSM-5 catalyst in protonated form having a Si/Al ratio of 50. Prior to the start of the reaction, the catalyst was calcined at 450°C in a flow of helium for 1 hour. Helium was passed through two toluene saturators connected in series and mixed with methyl chloride gas so as to have a toluene/methyl chloride ratio of 1. The reactants were passed through the catalyst bed maintained at 375°C, under atmospheric pressure. The weight hourly space velocities (WHSV) of toluene and methyl chloride were varied from 0.29 to 1.77 h⁻¹ and from 0.16 to 0.97 h⁻¹, respectively. The products

formed were analyzed by gas chromatography. The product distribution obtained with weight hourly space velocities of toluene and methyl chloride of 0.59 h^{-1} and 0.32 h^{-1} , respectively, is shown in Table 1.

5

TABLE 1

Si/Al ratio	50
Time on Stream (minutes)	180
WHSV (h^{-1})	
- Methyl Chloride	0.32
- Toluene	0.59
Conversion (%)	
- Methyl Chloride	41.4
- Toluene	14.7

TABLE 1 (cont'd)

Hydrocarbon Distribution (wt.%)	
C ₁ -C ₄ Aliphatics	24.0
C ₅₊ Aliphatics	2.6
Benzene	0.4
Ethylbenzene	0.2
p-Xylene	57.5
m-Xylene	5.5
o-Xylene	1.9
3-Methylethylbenzene	5.7
4-Methylethylbenzene	0.9
2-Methylethylbenzene	0.0
1,3,5-Trimethylbenzene	0.0
1,2,4-Trimethylbenzene	1.5
1,2,3-Trimethylbenzene	0.0
C ₁₀ Aromatics	0.0
Total Xylenes	64.9
Isomer distribution (%)	
p-xylene	88.6
m-xylene	8.5
o-xylene	2.9
Total Ethyltoluenes	6.6
Total Trimethylbenzenes	1.5

EXAMPLE 2

The reactor of Example 1 was charged with 0.5 g of protonated ZSM-5 catalyst having a Si/Al ratio of 50 and methylation of toluene with methyl chloride was carried out under the same temperature and pressure conditions as in Example 1. The product distribution obtained at 375°C with weight hourly space velocities of 0.30 h⁻¹ and 0.16 h⁻¹ for toluene and methyl chloride, respectively, is shown in Table 2.

10

TABLE 2

Si/Al ratio	50
Time on Stream (minutes)	240
WHSV (h ⁻¹)	
- Methyl Chloride	0.16
- Toluene	0.30
Conversion (%)	
- Methyl Chloride	78.5
- Toluene	25.5

TABLE 2 (cont'd)

Hydrocarbon Distribution (wt.%)	
C ₁ -C ₄ Aliphatics	25.7
C ₅ + Aliphatics	1.9
Benzene	0.5
Ethylbenzene	0.2
p-Xylene	50.0
m-Xylene	8.5
o-Xylene	2.7
3-Methylethylbenzene	6.4
4-Methylethylbenzene	1.8
2-Methylethylbenzene	0.0
1,3,5-Trimethylbenzene	0.0
1,2,4-Trimethylbenzene	2.1
1,2,3-Trimethylbenzene	0.0
C ₁₀ Aromatics	0.1
Total Xylenes	61.2
Isomer distribution (%)	
p-xylene	81.7
m-xylene	13.9
o-xylene	4.4
Total Ethyltoluenes	8.2
Total Trimethylbenzenes	2.1

5 **EXAMPLE 3**

Methylation of toluene with methyl chloride was carried out using protonated ZSM-5 zeolites with

Si/Al ratios of 25 and 36 under the same temperature and pressure conditions as in Example 1. The weight hourly space velocities of toluene and methyl chloride were 0.59 h^{-1} and 0.32 h^{-1} , respectively. A comparison of product distributions obtained with the two catalysts at 375°C is shown in Table 3.

TABLE 3

Si/Al ratio	25	36
Time on Stream (minutes)	175	180
WHSV (h^{-1})		
- Methyl Chloride	0.32	0.32
- Toluene	0.59	0.59
Conversion (%)		
- Methyl Chloride	82.1	86.6
- Toluene	32.2	37.0

10

TABLE 3 (cont'd)

Hydrocarbon Distribution (wt.%)		
C ₁ -C ₄ Aliphatics	14.8	14.6
C ₅ + Aliphatics	0.6	1.3
Benzene	0.7	0.5
Ethylbenzene	0.2	0.2
p-Xylene	22.1	18.3
m-Xylene	27.4	25.4
o-Xylene	10.5	12.9
3-Methylethylbenzene	3.0	2.7
4-Methylethylbenzene	4.8	4.2
2-Methylethylbenzene	0.3	0.3
1,3,5-Trimethylbenzene	0.2	0.5
1,2,4-Trimethylbenzene	12.7	18.9
1,2,3-Trimethylbenzene	0.0	0.1
C ₁₀ Aromatics	2.8	0.04
Total Xylenes	60.0	56.6
Isomer distribution (%)		
p-xylene	36.8	32.3
m-xylene	45.7	44.9
o-xylene	17.5	22.8
Total Ethyltoluenes	8.1	7.2
Total Trimethylbenzenes	12.9	19.5

5 Although the para-xylene selectivity is low, high conversions of toluene and methyl chloride are achieved. Protonated ZSM-5 zeolites with low Si/Al

ratios (i.e. 25 and 36) also produce trimethylbenzenes as the major hydrocarbon by-products. These trimethylbenzenes, whose octane numbers are high, can be used as octane boosters in gasoline.

5 **EXAMPLE 4**

Methylation of toluene with methyl chloride was also carried out using a protonated ZSM-5 zeolite catalyst modified with 10 wt.% of 12-tungstophosphoric acid and having a Si/Al ratio of 36. The modified
 10 zeolite catalyst was tested for its activity and selectivity in the methylation of toluene at 350°C and atmospheric pressure. The activity and product selectivity of the modified zeolite catalyst were compared with those of an unmodified, protonated ZSM-5
 15 zeolite catalyst having the same Si/Al ratio. A comparison of the product distributions obtained with the two catalysts at 350°C is shown in Table 4.

TABLE 4

20

Si/Al ratio	36 (modified)	36 (unmodified)
Time on Stream (minutes)	180	185
WHSV (h ⁻¹)		
- Methyl Chloride	0.32	0.32
- Toluene	0.59	0.59
Conversion (%)		
- Methyl Chloride	66.8	80.3
- Toluene	24.9	34.4

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TABLE 4 (cont'd)

Hydrocarbon Distribution (wt.%)		
C ₁ -C ₄ Aliphatics	17.9	14.9
C ₅ + Aliphatics	1.0	0.5
Benzene	0.4	0.5
Ethylbenzene	0.2	0.5
p-Xylene	24.5	18.5
m-Xylene	20.9	24.2
o-Xylene	8.8	10.5
3-Methylethylbenzene	3.7	3.1
4-Methylethylbenzene	4.5	5.1
2-Methylethylbenzene	0.2	0.3
1,3,5-Trimethylbenzene	0.2	0.4
1,2,4-Trimethylbenzene	17.1	20.2
1,2,3-Trimethylbenzene	0.0	1.1
C ₁₀ Aromatics	0.5	0.2
Total Xylenes	54.2	53.2
Isomer distribution (%)		
p-xylene	45.2	34.8
m-xylene	38.6	45.5
o-xylene	16.2	19.7
Total Ethyltoluenes	8.4	8.5
Total Trimethylbenzenes	17.3	21.7

EXAMPLE 5

The reactor of Example 1 was charged with 0.2 g of protonated ZSM-5 zeolite catalyst having a Si/Al ratio of 50 and the methylation of toluene was carried out under the same temperature and pressure conditions as in Example 1. The product distribution obtained at 375°C with weight hourly space velocities of toluene and methyl chloride of 1.47 h⁻¹ and 0.81 h⁻¹, respectively, is shown in Table 5.

10

TABLE 5

Si/Al ratio	50
Time on Stream (minutes)	285
WHSV (h ⁻¹)	
- Methyl Chloride	0.81
- Toluene	1.47
Conversion (%)	
- Methyl Chloride	14.8
- Toluene	10.2

TABLE 5 (cont'd)

Hydrocarbon Distribution (wt.%)	
C ₁ -C ₄ Aliphatics	20.8
C ₅₊ Aliphatics	4.0
Benzene	0.4
Ethylbenzene	0.1
p-Xylene	64.4
m-Xylene	3.8
o-Xylene	1.5
3-Methylethylbenzene	3.6
4-Methylethylbenzene	0.2
2-Methylethylbenzene	0.0
1,3,5-Trimethylbenzene	0.0
1,2,4-Trimethylbenzene	1.2
1,2,3-Trimethylbenzene	0.0
C ₁₀ Aromatics	0.0
Total Xylenes	69.7
Isomer distribution (%)	
p-xylene	92.4
m-xylene	5.4
o-xylene	2.1
Total Ethyltoluenes	3.8
Total Trimethylbenzenes	1.2

The embodiments of the invention, in which an exclusive property or privilege is claimed are defined as follows:

1. A process for the selective methylation of toluene to produce para-xylene, which comprises reacting toluene with a methyl halide at a temperature ranging from about 100 to about 500°C and a pressure ranging from about 1 to about 10 atmospheres, in the presence of:

a) an unmodified, shape-selective zeolite catalyst in protonated form having a Si/Al ratio of about 50, or

b) a heteropolyacid modified, shape-selective zeolite catalyst in protonated form having a Si/Al ratio of at least about 25 and less than about 50.

2. A process as claimed in claim 1, wherein said methyl halide is selected from the group consisting of methyl chloride, methyl bromide and methyl iodide.

3. A process as claimed in claim 2, wherein said methyl halide is methyl chloride.

4. A process as claimed in claim 3, wherein said methyl chloride is produced by chlorination of methane or natural gas.

5. A process as claimed in claim 4, wherein said methyl chloride is produced by oxyhydrochlorination of natural gas.

6. A process as claimed in claim 1, wherein said reaction is carried out at a temperature of about 300 to about 400°C.
7. A process as claimed in claim 1 or 6, wherein said reaction is carried out at atmospheric pressure.
8. A process as claimed in claim 1, wherein the toluene and methyl halide are reacted in a ratio of toluene/methyl halide ranging from about 0.1 to about 10.
9. A process as claimed in claim 8, wherein said toluene/methyl halide ratio is about 1.
10. A process as claimed in claim 1, wherein the reaction is carried out utilizing a weight hourly space velocity of each of toluene and methyl halide in the range of about 0.01 to about 10 h⁻¹.
11. A process as claimed in claim 10, wherein said weight hourly space velocity ranges from about 0.1 to about 1 h⁻¹.
12. A process as claimed in claim 1, wherein said reaction is carried out in the presence of said unmodified zeolite catalyst.
13. A process as claimed in claim 12, wherein said zeolite catalyst has a degree of H⁺ exchange ranging from about 10 to about 100%.

14. A process as claimed in claim 1, wherein said reaction is carried out in the presence of said heteropolyacid modified zeolite catalyst.

15. A process as claimed in claim 14, wherein said zeolite catalyst is modified with a heteropoly acid selected from the group consisting of 12-tungstophosphoric acid, 12-tungstosilicic acid and 12-molybdophosphoric acid.

16. A process as claimed in claim 14, wherein the modified zeolite catalyst comprises from about 0.5 to about 25 wt.% of said heteropoly acid.

17. A process as claimed in claim 16, wherein said modified zeolite catalyst comprises about 10 wt.% of 12-tungstophosphoric acid.

18. A process for the selective methylation of toluene to produce para-xylene, which comprises the steps of:

a) chlorinating natural gas to produce methyl chloride;

b) reacting the methyl chloride obtained in step (a) with toluene at a temperature ranging from about 100 to about 500°C and a pressure ranging from about 1 to about 10 atmospheres, in the presence of an unmodified shape-selective zeolite catalyst in protonated form having a Si/Al ratio of about 50, to obtain a product mixture rich in para-xylene; and

c) extracting the para-xylene from the product mixture obtained in step (b).

19. A process as claimed in claim 18, wherein step (b) is carried out at a temperature of about 300 to about 400°C and at atmospheric pressure, and wherein said zeolite catalyst has a degree of H⁺ exchange of about 10 to about 100%.

20. A process for the selective methylation of toluene to produce para-xylene, which comprises the steps of:

a) chlorinating natural gas to produce methyl chloride;

b) reacting the methyl chloride obtained in step (a) with toluene at a temperature ranging from about 100 to 500°C and a pressure ranging from about 1 to about 10 atmospheres, in the presence of a shape-selective zeolite catalyst in protonated form having a Si/Al ratio of at least about 25 and less than about 50, wherein said zeolite catalyst is modified with a heteropoly acid selected from the group consisting of 12-tungstophosphoric acid, 12-tungstosilicic acid and 12-molybdophosphoric acid, the modified zeolite catalyst comprising from about 0.5 to about 25 wt.% of said heteropoly acid, to obtain a product mixture rich in para-xylene; and

c) extracting the para-xylene from the product mixture obtained in step (b).

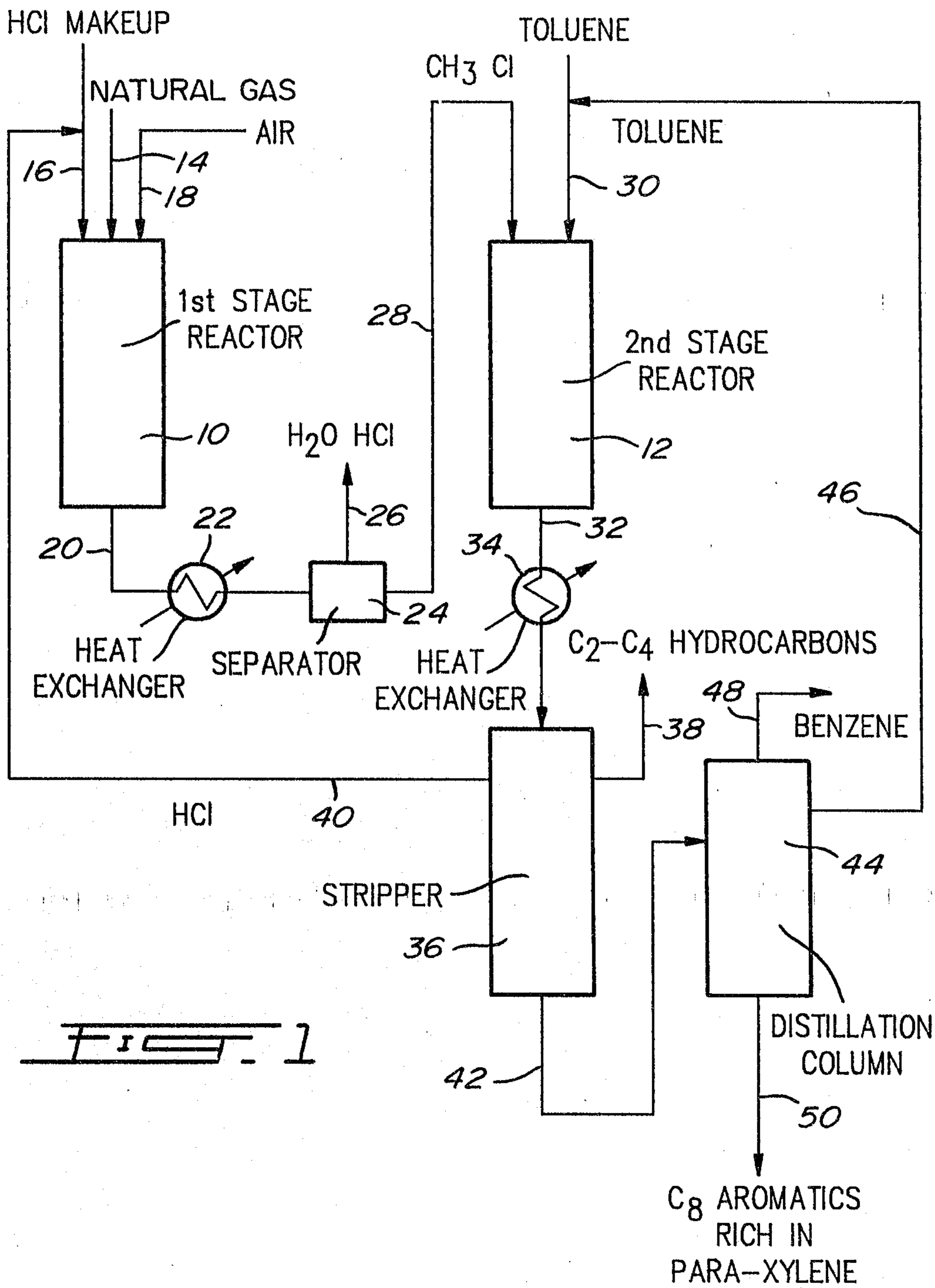


FIG. 1

PATENT AGENTS

Swabeys Ogilvy Renault