



(51) International Patent Classification:

C07C 5/22 (2006.01)

C07C 7/00 (2006.01)

(21) International Application Number:

PCT/IN2013/000651

(22) International Filing Date:

25 October 2013 (25.10.2013)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

2754/MUM/2013 23 August 2013 (23.08.2013)

IN

(71) Applicant: HINDUSTAN PETROLEUM CORPORATION LIMITED [IN/IN]; Petroleum House, 17 Jamshedji Tata Road, Churchgate, Mumbai 400020, Maharashtra (IN).

(72) Inventors: RAVISHANKAR, Raman; Corporate R&D, HPCL, 176, Adarsh EcoPlace, EPIP Zone II, Whitefield, Bangalore 560066, Karnataka (IN). PEDDY, Venkata, Chalapathi, Rao; Corporate R&D, HPCL, 176, Adarsh EcoPlace, EPIP Zone II, Whitefield, Bangalore 560066, Karnataka (IN). NETTEM, Venkateswarlu, Choudary; Corporate R&D, HPCL, 176, Adarsh EcoPlace, EPIP Zone II, Whitefield, Bangalore 560066, Karnataka (IN). SHANBHAG, Ganapati; Corporate R&D, HPCL, 176, Adarsh EcoPlace, EPIP Zone II, Whitefield, Bangalore 560066, Karnataka (IN). MARAKATTI, Vijaykumar; Materials Science Division, Poomaprajna Institute of Scientific Research (PPISR), Poomaprajnapura, Post: Bidalur, Ta: Devanahalli, Bangalore 562110, Karnataka (IN). HALGER, Anand; Materials Science Division, Poomaprajna Institute of Scientific Research (PPISR), Poomaprajnapura, Post: Bidalur, Ta: Devanahalli, Bangalore 562110, Karnataka (IN). GANDHAM Sriganesh; Corporate R&D,

HPCL, First Floor, 176, Adarsh EcoPlace, EPIP Zone II, Whitefield, Bangalore 560066, Karnataka (IN).

(74) Agent: MOHAN, Dewan; R. K. Dewan & Company, Trade Mark & Patent Attorneys, Podar Chambers, S.A. Brelvi Road, Fort, Mumbai 400001 Maharashtra (IN).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

- as to the identity of the inventor (Rule 4.17(i))
- of inventorship (Rule 4.17(iv))

Published:

- with international search report (Art. 21(3))

(54) Title: A PROCESS FOR THE PREPARATION OF ISOMERS OF XYLENE

(57) Abstract: The present disclosure relates to a process for the preparation of isomers of xylene. The process includes method step of contacting an activated alkylation catalyst composite with toluene and methanol in the presence of an inert gas, at a temperature of 300 to 500°C to obtain isomers of xylene. The alkylation catalyst composite used in accordance with the present disclosure comprises a molecular sieve loaded with at least one metal ion. The metal loaded on the molecular sieve is at least one alkali earth metal selected from the group consisting of barium, strontium, magnesium and calcium.



A PROCESS FOR THE PREPARATION OF ISOMERS OF XYLENE

FIELD OF THE DISCLOSURE:

The present disclosure related to a process for the preparation of isomers of xylene.

BACKGROUND:

Xylene is monocyclic aromatic compound with two methyl groups attached to the benzene ring. It exists in three isomeric forms: ortho, meta and para-xylene. Mostly, the individual isomers of xylene are separated and consumed in specific end-uses. Ortho-xylene is used primarily in the synthesis of phthalic acid, unsaturated polyester resins, alkyd resins; meta-xylene is key component for the synthesis of isophthalic acid and para-xylene is an important precursor to terephthalic acid and dimethyl terephthalate.

Usually, xylene is synthesized by the Friedel-Crafts alkylation reaction. However, alkylation catalysts such as AlCl_3 , HF and H_2SO_4 employed in the Friedel-Crafts alkylation reaction have found to be environmentally hazardous. Therefore, in recent years, molecular sieve catalyst such as zeolites and silico aluminophosphate have attracted attention as alkylation catalysts, typically, due to their higher acidic properties, potential for regeneration and easy of separation from the reaction mixture.

However, use of such acidic alkylation catalysts in alkylation of toluene produces mix-xylenes, containing predominantly meta-xylene and para-xylene with very minor amount of ortho-xylene. While, the alkylation of toluene in the presence of basic alkylation catalyst such as Na-X-zeolite, Na-Y-zeolite, Na-beta-zeolite Na-ZSM-5 zeolite, Cs-X zeolite, Ba zeolite, and Rb-X zeolite predominantly, produces ethyl benzene and styrene due to side chain alkylation reaction.

Therefore, there is need to develop a simple and economic process for the preparation of isomers of xylene, particularly ortho-xylene using the basic alkylation catalyst.

OBJECTS

Some of the objects of the present disclosure, which at least one embodiment is able to achieve, are discussed herein below.

It is an object of the present disclosure to provide safe and economic process for the preparation of alkyl aromatic compounds using the basic alkylation catalyst composite.

It is another object of the present disclosure to provide safe and economic process for the preparation of isomers of xylene using the basic alkylation catalyst composite.

It is a further object of the present disclosure to provide a selective process for the preparation of ortho-xylene using the basic alkylation catalyst composite.

Other objects and advantages of the present disclosure will be more apparent from the following description when read in conjunction with the accompanying drawing, which are not intended to limit the scope of the present disclosure.

Definitions:

As used in the present specification, the term 'molecular sieve' is used to define class of materials that exhibits selected sorption properties.

BRIEF DESCRIPTION OF THE ACCOMPANYING DRAWING

Figure 1: illustrates the XRD for the alkylation catalyst composite of the present disclosure, in which A represents XRD for the Ca-X zeolite catalyst composite, B represents XRD for the Mg-X zeolite catalyst composite, C represents XRD for the Sr-X zeolite catalyst composite and D represents XRD for the Ba-X zeolite catalyst composite.

Figure 2: illustrates the XRD for the Sr ion exchanged X zeolite catalyst composite of the present disclosure, in which:

A represents XRD for the Sr -X zeolite catalyst composite obtained after refluxing Na X-zeolite with strontium nitrate;

B represents XRD for the Sr - X zeolite catalyst composite obtained after repeating the method step of refluxing Na X-zeolite with strontium nitrate two times; and

C represents XRD for the Sr - X zeolite catalyst composite obtained after repeating the method step of refluxing Na X-zeolite with strontium nitrate three times.

Figure 3: illustrates amount of toluene alkylated using Mg-X zeolite catalyst composite, Ca-X zeolite catalyst composite, Sr-X zeolite catalyst composite and Ba-X zeolite catalyst composite of the present disclosure. In which A represents percent conversion of toluene, B represents percent alkylation of toluene to m-xylene, C represents percent alkylation of toluene to p-xylene and C represents percent alkylation of toluene to o- xylene.

SUMMARY:

In accordance with one aspect of the present disclosure there is provided a process for the preparation of isomers of xylene; said process comprising the following steps:

- i. obtaining an alkylation catalyst composite comprising a molecular sieve loaded with at least one metal ion;
- ii. activating the alkylation catalyst composite at a temperature of 450 to 650°C for a time period of 30 min to 2 hrs. in a reactor to obtain an activated alkylation catalyst composite; wherein the temperature for activating the alkylation catalyst composite is attained by heating the reactor at a rate of 4 to 10°C per minute; and
- iii. contacting the activated alkylation catalyst composite with toluene and methanol in the presence of an inert gas, at a temperature of 300 to 500°C to obtain a reaction mixture comprising isomers of xylene; wherein the mass of the ortho-xylene in said reaction mixture is greater than the individual mass of para-xylene and meta-xylene.

Typically, the molecular sieve is at least one zeolite selected from the group consisting of X-zeolite, Y-zeolite, beta-zeolite, ZSM-5 zeolite mordenite, ZSM-48, ZSM-22, ZSM-23, ZSM-57 and MCM-22.

Typically, the molecular sieve is at least one silico aluminophosphate (SAPO) selected from the group consisting of SAPO-5, SAPO-11, SAPO-17, SAPO-18, SAPO-44, SAPO-34 and SAPO-48.

Typically, the metal is at least one selected from the group consisting of group I elements, group II elements, group III elements, lanthanides and transition metals.

Typically, the metal is at least one selected from the group consisting of barium, strontium, magnesium and calcium.

Typically, the ratio of toluene to methanol ranges between 1:1 and 4:1.

Typically, the flow rate of toluene is maintained at a weight hourly space velocity of 1 to 5 per hr. of the activated alkylation catalyst composite.

Typically, the inert gas is at least one selected from the group consisting of nitrogen, argon and helium.

Typically, the flow rate of the inert gas ranges between 5 and 15 per min.

DETAILED DESCRIPTION:

Alkylation of toluene using the acidic alkylation catalyst predominantly produces meta and para isomers of xylene, while the basic alkylation catalyst produces ethyl benzene and styrene. Therefore, with the view of increasing the yield of ortho-xylene, the inventors of the present disclosure have conducted several experiments and trials using number of alkylation catalysts. The inventors surprisingly found that the basic alkylation catalyst composite comprising molecular sieve loaded with at least one metal ion can selectively be used for the preparation of the isomers of xylene typically, ortho-xylene. Accordingly, the inventors of the present disclosure have developed a novel process for alkylation of toluene using the basic alkylation catalyst composite.

In accordance with one aspect of the present disclosure there is provided a process for the preparation of isomers of xylene.

In the initial step, the alkylation catalyst composite comprising a molecular sieve loaded with at least one metal ion is activated at a temperature of 450 to 650°C for a time period of 30 min to 2 hrs. in a reactor to obtain an activated alkylation catalyst

composite. The temperature for activating the alkylation catalyst composite is attained by heating the reactor at a rate of 4 to 10°C per minute.

In accordance with one embodiment of the present disclosure the molecular sieve may be zeolite selected from the group consisting of X-zeolite, Y-zeolite, beta-zeolite, ZSM-5 zeolite mordenite, ZSM-48, ZSM-22, ZSM-23, ZSM-57, MCM-22 and mixtures thereof.

In accordance with another embodiment of the present disclosure the molecular sieve may be silico aluminophosphate (SAPO) selected from the group consisting of SAPO-5, SAPO-11, SAPO-17, SAPO-18, SAPO-44, SAPO-34, SAPO-48 and combinations thereof.

Typically, the metal loaded on molecular sieve is at least one selected from the group consisting of group I elements, group II elements, group III elements, lanthanides and transition metals.

Typically, the metal loaded on molecular sieve is at least one selected from the group consisting of barium, strontium, magnesium and calcium.

In the next step, the activated alkylation catalyst composite is contacted with toluene and methanol at a temperature of 300 to 500°C to obtain a reaction mixture comprising isomers of xylene as ortho-xylene, meta-xylene and para-xylene.

The mass of ortho-xylene present in the reaction mixture is greater the individual mass of para-xylene and meta-xylene.

The ratio of toluene to methanol is maintained in the range of 1:1 to 4:1 and the flow rate of toluene is maintained at a weight hourly space velocity of 1 to 5 per hr. of the activated catalyst.

The method step of contacting the activated alkylation catalyst composite with toluene and methanol is carried out in the presence of inert gas selected from the group consisting of nitrogen, argon, helium and combinations thereof. The flow rate of inert gas is maintained in the range of 5 to 15 ml/min.

The present disclosure is further described in light of the following examples which are set forth for illustration purpose only and not to be construed for limiting the scope of the disclosure.

Example 1: Preparation of Ba-X zeolite using Na-X zeolites:**Step 1: Preparation of Na-X zeolite:**

5gm of zeolite was treated with 20 liter of 0.5 M aqueous solution of sodium nitrate (NaNO_3) under reflux for 8 hrs, followed by filtration, washing with water until the filtrate became free from sodium ions, drying at 120 °C for 8 h and calcination at 550 °C for 4 h in air. The ratio of aqueous solution of sodium nitrate to zeolite was maintained as 10: 1. The procedure was repeated twice to obtain Na-X zeolites.

Step II- Preparation of an alkylation catalyst composite (Ba-X zeolite catalyst composite) using Na-X zeolite:

The Na-X zeolite was treated with 0.5 M of barium acetate solution using the method described in step I to obtain a Ba-X zeolite. In this process the sodium nitrate is replaced with barium acetate.

Step III- Preparation of isomers of xylene using Ba-X zeolite catalyst composite:

2 g of Ba-X zeolites catalyst composite of 0.8 to 1.7 mm mesh size was taken in a quartz micro reactor. Temperature in the reactor was ramped with 8 °C/ min to 500 °C. Catalyst was activated in presence of air for a time period of 1 hr. Then the temperature of the activated catalyst was brought down to 420°C. Feed of Toluene and methanol (4:1) with a weight hourly space velocity (WHSV) (toluene) = 2.5 h^{-1} was fed into pre-heater with a syringe pump and nitrogen was fed with calibrated Rota meter with the flow of 10 ml/ min. Products were cooled in condenser maintained at 2°C and products are collected in gas liquid separator maintained at 5°C. Products were analyzed through gas chromatograph equipped with FID using a carbowax (polar) column of 60m x 0.25 μm x 0.25 mm.

Table 1:

	1hr.	2hrs.	3 hrs.	4hrs.
Product distribution (wt%)				
Benzene	0.01	0.007	0.04	0.005

Toluene	98.60	98.67	98.78	98.93
Ethyl benzene	0.03	0.024	0.024	0.023
<i>p</i> -xylene	0.26	0.26	0.23	0.21
<i>m</i> - xylene	0.25	0.23	0.20	0.19
<i>o</i> - xylene	0.78	0.77	0.68	0.60
Styrene	0.01	0.01	0.01	0.005
Trimethyl benzene	0.02	0.02	0.02	0.02
Others	0.03	0.02	0.01	0.01
Performance (wt%)				
Toluene conversion	1.4	1.3	1.2	1.1
Styrene selectivity	0.8	0.8	1	0.4
Ethyl benzene selectivity	2	2.1	2	2
Mixed xylene selectivity	92.3	95.4	92.3	90.9

Example 2: Preparation of an alkylation catalyst composite (Ca-X zeolite catalyst composite) using Na-X zeolite:

The Na-X zeolite was treated with 0.5 M of calcium nitrate (CaNO_3) solution using the step-I of Example 1 to obtain a Ca-X zeolite. In this process sodium nitrate is replaced with calcium nitrate.

Preparation of isomers of xylene using Ca-X zeolite catalyst composite:

The isomers of xylene were prepared by employing the procedure described in the Example 1. In this process Ba-X zeolites catalyst composite is replaced with Ca-X zeolite catalyst composite

Table 2:

	1hr.	2hrs.	3 hrs.	4hrs.
Product distribution (wt%)				
Benzene	0.26	0.36	0.44	0.51

Toluene	89.43	87.59	86.94	87.99
Ethyl benzene	0.033	0.062	0.08	0.08
<i>p</i> -xylene	2.55	3.35	3.66	3.49
<i>m</i> - xylene	2.28	2.70	2.93	2.83
<i>o</i> - xylene	3.98	3.43	3.06	2.65
Styrene	0.08	0.13	0.14	0.12
Trimethyl benzene	0.87	1.26	1.30	1.08
Others	0.51	1.11	1.46	1.23
Performance (wt%)				
Toluene conversion	10.57	12.42	13.07	12.02
Styrene selectivity	0.7	1.0	1.0	1.0
Ethyl benzene selectivity	0.3	0.5	0.6	0.7
Mixed xylene selectivity	83.1	76.24	73.75	74.65

Example 3: Preparation of an alkylation catalyst composite (Mg-X zeolite catalyst composite) using Na-X zeolite:

The Na-X zeolite was treated with 0.5 M of Magnesium nitrate (MgNO_3) solution using the step-I of Example 1 to obtain a Mg-X zeolite. In this process sodium nitrate is replaced with Magnesium nitrate.

Preparation of isomers of xylene using Mg -X zeolite catalyst composite:

The isomers of xylene were prepared by employing the procedure described in the Example 1. In this process Ba-X zeolite catalyst composite is replaced with Mg -X zeolites catalyst composite.

Table 3:

	1hr.	2hrs.	3 hrs.
Product distribution (wt%)			
Benzene	0.45	0.42	0.48
Toluene	90.4	90.44	89.28

Ethyl benzene	0.05	0.06	0.07
p-xylene	2.90	2.86	3.29
m- xylene	2.50	2.450	2.76
o- xylene	2.15	2.153	2.34
Styrene	0.110	0.103	0.11
Trimethyl benzene	0.780	0.785	0.93
Others	0.730	0.725	0.73
Performance (wt%)			
Toluene conversion	9.6	9.56	10.73
Styrene selectivity	1.1	1.0	1.0
Ethyl benzene selectivity	0.5	0.5	0.6
Mixed xylene selectivity	78.64	78	78.2

Example 4: Preparation of the alkylation catalyst composite (Sr-X zeolite catalyst composite) using Na-X zeolites:

The Na-X zeolite was treated with 0.5 M of Strontium nitrate ($\text{Sr}(\text{NO}_3)_2$) solution using Step-I of Example 1 to obtain a Sr -X zeolite. In this process sodium nitrate is replaced with Strontium nitrate.

Preparation of isomers of xylene using Sr-X zeolite catalyst composite:

The isomers of xylene were prepared by employing the procedure described in the Example 1. In this process Ba-X zeolite catalyst composite is replaced with Sr-X zeolites catalyst composite.

Table 4:

	1hr.	2hrs.	3 hrs.	4hrs.
Product distribution (wt %)				
Benzene	0.058	0.054	0.094	0.10
Toluene	88.70	89.17	87.97	88.77
Ethyl benzene	0.022	0.03	0.037	0.05

p-xylene	2.48	2.21	2.48	2.43
m- xylene	2.10	1.86	2.03	1.93
o- xylene	5.46	4.62	4.33	3.87
Styrene	0.06	0.10	0.10	0.14
Trimethyl benzene	1.1	1.04	1.23	1.12
Others	0.97	0.91	1.72	1.60
Performance (wt%)				
Toluene conversion	11.3	10.83	12.04	11.23
Styrene selectivity	0.5	0.1	0.8	1.2
Ethyl benzene selectivity	0.1	0.2	0.3	0.4
Mixed xylene selectivity	88.8	80	73.3	73.1

Example 5: Preparation of Sr-beta zeolite catalyst composite:

Step I Preparation Na-beta zeolites Catalyst:

5 gm of H-Beta zeolite was treated with 20 ml of 0.5 M aqueous solution of sodium nitrate under reflux for 8 hrs., followed by filtration, washing with water until the filtrate became free from sodium ions, drying at 120 °C for 8 h and calcination at 550 °C for 4 h in air. The ratio of sodium nitrate to zeolite was maintained as 10: 1. The procedure was repeated twice to obtain Na- Beta zeolite.

Step II Preparation of an alkylation catalyst composite (Sr-beta zeolite catalyst composite) using Na-beta zeolites:

The Sr -beta zeolite catalyst was prepared by using the procedure described for the preparation of Na-beta zeolites (Step I). In this process sodium nitrate is replaced with Strontium nitrate ($\text{Sr}(\text{NO}_3)_2$).

Preparation of isomers of xylene using Sr-beta zeolite catalyst composite:

The isomers of xylene were prepared by employing the procedure described in the Example 1. In this process Ba-X zeolite catalyst composite is replaced with Sr-X beta zeolites catalyst composite.

Table 5:

	1hr.	2hrs.	3 hrs.	4hrs.
Product distribution (wt%)				
Benzene	7.55	7.84	7.20	6.43
Toluene	59.02	58.60	57.88	57.94
Ethyl benzene	0.24	0.263	0.28	0.28
p-xylene	6.52	6.50	6.72	6.74
m- xylene	14.42	14.34	14.81	14.89
o- xylene	6.28	6.24	6.45	6.49
Trimethyl benzene	3.08	3.09	3.35	3.5
Others	2.88	3.11	3.28	3.7
Performance (wt%)				
Toluene conversion	41.0	41.4	42.14	42.1
Mixed xylene selectivity	66.36	65.45	66.3	66.7
P-Xylene selectivity	24	24	23.9	24
m- xylene selectivity	53	52.9	52.87	52.9
o-xylene selectivity	23	23	23	23

Example 6: Preparation of an alkylation catalyst composite (Sr- ZSM-5 zeolite catalyst composite) using Na-ZSM-5 zeolite:

The Sr- ZSM-5 zeolite was prepared by using the Step-I of the Example 6, in this process H-Beta zeolite is replaced with H-ZSM-5 zeolite.

Preparation of isomers of xylene using Sr- ZSM-5 zeolite catalyst composite:

The isomers of xylene were prepared by employing the procedure described in the Example 1. In this process Ba-X zeolite catalyst composite is replaced with Sr- ZSM-5 zeolites catalyst composite.

Table 6:

	1hr.	2hrs.	3 hrs.	4hrs.
Product distribution (wt%)				
Benzene	0.29	0.33	0.34	0.32
Toluene	85.72	84.08	83.26	83.73
Ethyl benzene	0.08	0.097	0.10	0.097
p-xylene	4.42	4.41	4.38	4.41
m- xylene	4.78	5.73	6.12	5.89
o- xylene	1.40	1.85	2.05	1.96
Trimethyl benzene	0.26	0.36	0.40	0.42
Others	3.03	3.13	3.35	3.15
Performance (wt%)				
Toluene conversion	14.27	16.0	16.74	16.27
Mixed xylene selectivity	74.2	74.8	74.9	75.3
P-Xylene selectivity	41.7	36.75	34.92	35.9
m- xylene selectivity	45	50.4	48.7	48
o-xylene selectivity	13.2	15.37	16.34	16.0

Example 7: Preparation of an alkylation catalyst composite (Sr- Y zeolite catalyst composite) using H-Y zeolite:

The Sr- ZSM-5 zeolite was prepared by using Step I of Example 6, in this process H-Beta zeolite is replaced with H-Y zeolite.

Preparation of isomers of xylene using Sr- Y zeolite catalyst composite:

The isomers of xylene were prepared by employing the procedure described in the Example 1. In this process Ba-X zeolite catalyst composite is replaced with Sr- Y zeolites catalyst composite

Table 7:

	1hr.	2hrs.	3 hrs.	4hrs.
Product distribution (wt%)				
Benzene	0.83	1.09	1.29	1.35
Toluene	84.90	82.7	80.93	81.86
Ethyl benzene	0.04	0.06	0.058	0.06
p-xylene	3.40	3.86	4.19	3.96
m- xylene	4.19	5.03	5.67	5.39
o- xylene	3.62	3.50	3.44	3.27
Trimethyl benzene	1.61	1.84	2.09	1.94
Others	1.40	1.88	2.40	2.17
Performance (wt%)				
Toluene conversion	15.11	17.3	19	18.15
Mixed xylene selectivity	74.1	71.5	69.4	69.4
P-Xylene selectivity	30.26	31.1	31.1	31.4
m- xylene selectivity	37.3	40.6	42.8	42.8
o-xylene selectivity	32.3	28.3	25.9	25.8

The catalytic activity of Sr- X zeolite catalyst composite was compared with the catalytic activity of Mg- X zeolite catalyst composite, Ca- X zeolite catalyst composite and Ba- X zeolite.(shown in Figure 3 and Table 8)

Table 8: Percent alkylation of toluene using the alkylation catalyst comprising Sr metal ion loaded zeolites.

Performance (wt%)	Sr-X	Sr-Y	Sr-ZSM-5	Sr-Beta
Toluene conversion	10.8	17.3	16	41.4
Mixed xylene selectivity	80.0	71.5	74.8	65.4
<i>p</i> -xylene selectivity	25.4	31.1	36.7	24.0
<i>m</i> -xylene selectivity	21.3	40.6	50.4	52.9
<i>o</i> -xylene selectivity	53.2	28.3	15.4	23

Characterization

XRD analysis:

1. The phase purity and crystalline properties of zeolite catalysts composite (Ca-X zeolite catalyst composite, Mg-X zeolite catalyst composite, Sr-X zeolite catalyst composite and Ba-X zeolite catalyst composite) were determined by the X-ray diffractometer instrument with Cu K α Source ($\lambda = 1.542 \text{ \AA}$). The zeolite catalysts were analyzed in the 2θ range of 5° to 70° with scanning rate of 0.02 degrees per second at temperature of 25°C . XRD pattern for zeolite catalysts shown in figure 1.
2. The phase purity and crystalline properties of Sr ion exchanged X zeolite was determined by the X-ray diffractometer instrument with Cu K α Source ($\lambda = 1.542 \text{ \AA}$). The zeolite catalyst was analyzed in the 2θ range of 10 to 70° with scanning rate of 0.02 degrees per second at temperature of 25°C . XRD pattern for Sr X zeolite shown in figure 2.

Atomic Absorption Spectrometry (AAS):

The percent sodium (Na) exchanged with the metal ions selected from the group consisting of magnesium(Mg), calcium(Ca), strontium(Sr) and barium(Ba) was determined by Atomic Absorption Spectrometry.

Table: 9

<i>S.No</i>	<i>Catalyst</i>	<i>Ion exchange (wt%)</i>
1.	Na-X zeolite	0.0
2	Mg-X zeolite	68.7
3.	Ca-X zeolite	92.8
4.	Sr-X zeolite	96.1
5.	Ba-X zeolite	93.8

Comparative Example 1:

The isomers of xylene were prepared by employing the procedure described in the Example 1. In this process Ba-X zeolite catalyst composite is replaced with commercially available Na-X zeolite catalyst.

Table 10:

	1hr.	2hrs.	3 hrs.	4hrs.
Product distribution (wt%)				
Benzene	0.023	0.010	0.008	0.008
Toluene	94.94	96.75	96.81	97.05
Ethyl benzene	0.067	0.077	0.08	0.09
p-xylene	0.715	0.61	0.65	0.60
m- xylene	0.63	0.51	0.53	0.50
o- xylene	1.69	1.49	1.57	1.46
Styrene	0.05	0.09	0.059	0.05
Trimethyl benzene	0.125	0.07	0.099	0.09
C ₉ -C ₁₀ aromatics	1.74	0.39	0.20	0.16
Performance (wt%)				
Toluene conversion	5.0	3.25	3.2	3.0
Styrene selectivity	1.0	2.86	1.8	1.5
Ethyl benzene selectivity	1.34	2.3	2.6	2.9
Mixed xylene selectivity	60.76	79.38	85	85

Comparative Example 2:

The isomers of xylene were prepared by employing the procedure described in the Example 1. In this process Ba-X zeolite catalyst composite is replaced with commercially available H-Beta and H-ZSM-5. The amount of the xylene produced by the Sr- X zeolite composite was then compared with amount of the xylene produced using H-Beta and HZSM-5

Table 11:

	Sr-X zeolite catalyst composite of the present disclosure	H-BETA	H-ZSM-5
Product distribution (wt%)			
Benzene	0.054	9.03	7.30
Toluene	89.17	68.66	60.24
Ethyl benzene	0.03	0.28	0.35
p-xylene	2.21	5.08	6.05
m- xylene	1.85	9.95	13.45
o- xylene	4.61	3.93	5.98
Others	0.91	3.03	6.6
Conversion and selectivity (wt%)			
Toluene conversion	10.83	31.34	39.76
Mixed xylene selectivity	80	60.54	63.9
p-xylene selectivity	25.4	26.4	23.5
m-xylene selectivity	21.3	52.7	52.89
o- xylene selectivity	52.9	20.8	23.5

The embodiments herein and the various features and advantageous details thereof are explained with reference to the non-limiting embodiments in the description. Descriptions of well-known components and processing techniques are omitted so as to not unnecessarily obscure the embodiments herein. The examples used herein are intended merely to facilitate an understanding of ways in which the embodiments herein may be practiced and to further enable those of skill in the art to practice the embodiments herein. Accordingly, the examples should not be construed as limiting the scope of the embodiments herein.

The foregoing description of the specific embodiments will so fully reveal the general nature of the embodiments herein that others can, by applying current knowledge,

readily modify and/or adapt for various applications such specific embodiments without departing from the generic concept, and, therefore, such adaptations and modifications should and are intended to be comprehended within the meaning and range of equivalents of the disclosed embodiments. It is to be understood that the phraseology or terminology employed herein is for the purpose of description and not of limitation. Therefore, while the embodiments herein have been described in terms of preferred embodiments, those skilled in the art will recognize that the embodiments herein can be practiced with modification within the spirit and scope of the embodiments as described herein.

Throughout this specification the word “comprise”, or variations such as “comprises” or “comprising”, will be understood to imply the inclusion of a stated element, integer or step, or group of elements, integers or steps, but not the exclusion of any other element, integer or step, or group of elements, integers or steps.

The use of the expression “at least” or “at least one” suggests the use of one or more elements or ingredients or quantities, as the use may be in the embodiment of the invention to achieve one or more of the desired objects or results.

The numerical values given for various physical parameters, dimensions and quantities are only approximate values and it is envisaged that the values higher than the numerical value assigned to the physical parameters, dimensions and quantities fall within the scope of the invention and the claims unless there is a statement in the specification to the contrary.

While certain embodiments of the inventions have been described, these embodiments have been presented by way of example only, and are not intended to limit the scope of the inventions. Variations or modifications in the process or compound or formulation or combination of this invention, within the scope of the invention, may occur to those skilled in the art upon reviewing the disclosure herein. Such variations or modifications are well within the spirit of this invention. The accompanying claims and their equivalents are intended to cover such forms or modifications as would fall within the scope and spirit of the invention.

Claims:

1. A process for the preparation of isomers of xylene; said process comprising the following steps:
 - i. obtaining an alkylation catalyst composite comprising a molecular sieve loaded with at least one metal ion;
 - ii. activating the alkylation catalyst composite at a temperature of 450 to 650°C for a time period of 30 min to 2 hrs. in a reactor to obtain an activated alkylation catalyst composite; wherein the temperature for activating the alkylation catalyst composite is attained by heating the reactor at a rate of 4 to 10°C per minute; and
 - iii. contacting the activated alkylation catalyst composite with toluene and methanol in the presence of an inert gas, at a temperature of 300 to 500°C to obtain a reaction mixture comprising isomers of xylene; wherein the mass of ortho-xylene in said reaction mixture is greater than the individual mass of para-xylene and meta-xylene.
2. The process as claimed in claim 1, wherein the molecular sieve is at least one zeolite selected from the group consisting of X-zeolite, Y-zeolite, beta-zeolite, ZSM-5 zeolite mordenite, ZSM-48, ZSM-22, ZSM-23, ZSM-57 and MCM-22.
3. The process as claimed in claim 1, wherein the molecular sieve is at least one silico aluminophosphate (SAPO) selected from the group consisting of SAPO-5, SAPO-11, SAPO-17, SAPO-18, SAPO-44, SAPO-34 and SAPO-48.
4. The process as claimed in claim 1, wherein the metal is at least one selected from the group consisting of group I elements, group II elements, group III elements, lanthanides and transition metals.
5. The process as claimed in claim 1, wherein the metal is at least one selected from the group consisting of barium, strontium, magnesium and calcium.

6. The process as claimed in claim 1, wherein the ratio of toluene to methanol ranges between 1:1 and 4:1.
7. The process as claimed in claim 1, wherein the flow rate of toluene is maintained at a weight hourly space velocity of 1 to 5 per hr. of the activated alkylation catalyst composite.
8. The process as claimed in claim 1, wherein the inert gas is at least one selected from the group consisting of nitrogen, argon and helium.
9. The process as claimed in claim 1, wherein the flow rate of the inert gas ranges between 5 and 15 per min.

1/2

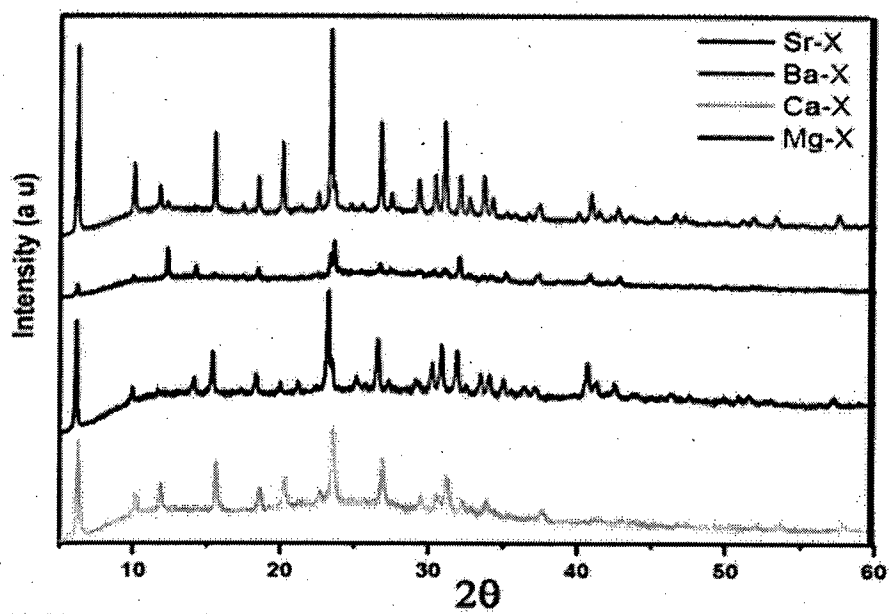


FIGURE 1

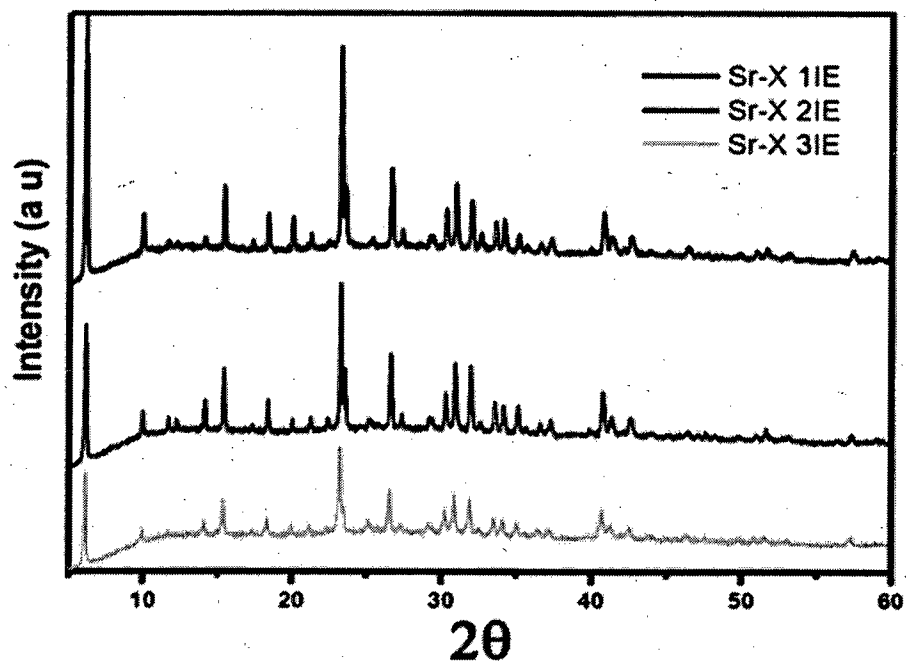


FIGURE 2

2/2

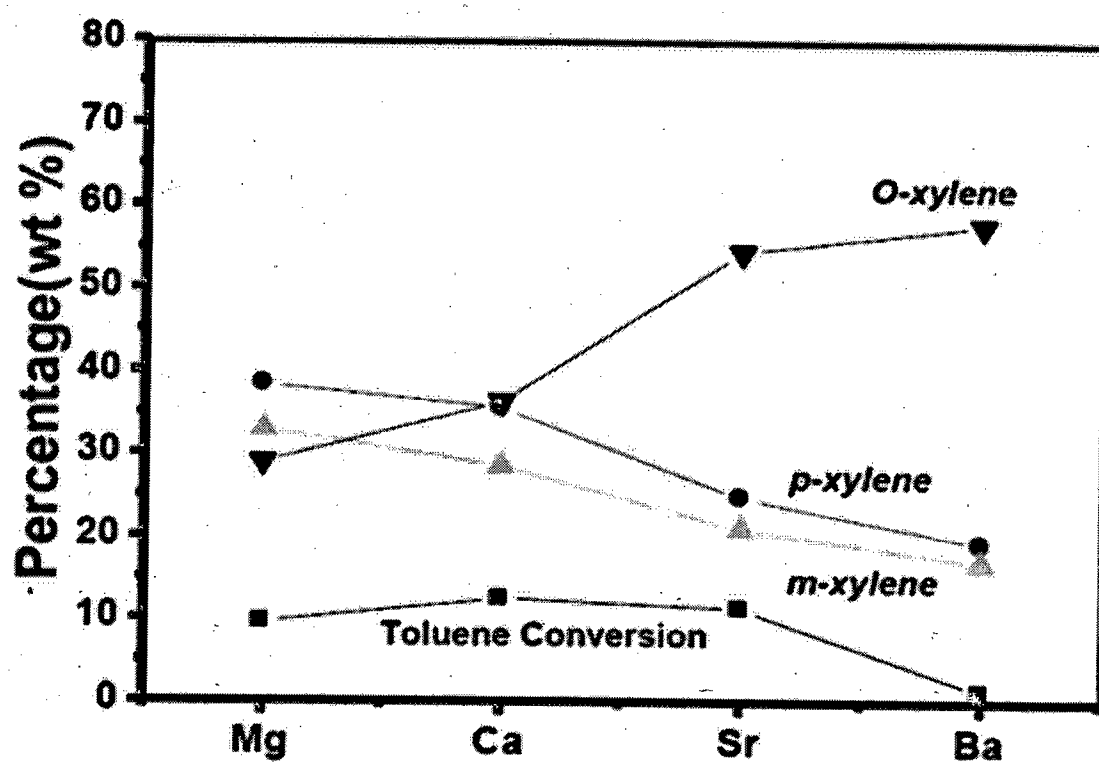


FIGURE 3

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - C07C 5/22; C07C 7/00 (2014.01)

USPC - 585/475,800,805

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)
USPC- 585/475Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
IPC(8)- C07C 5/22; C07C 7/00 (2014.01)
USPC- 585/475,800,805Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
PatBase (PGPB, USPT, USOC, EPAB, JPAB, DWPI, TDBD), FreePatentsOnline (US Pat, PgPub, EPO, JPO, WIPO, NPL),
GoogleScholar (PL, NPL); search terms: somers xylene zeolite catalyst zsm Isomer xylene alkylation catalyst composite molecular sieve
metal ion activating temperature 450 650 oC activated heating reactor toluene methanol inert gas reaction mi

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3,965,208 A (Butter et al.) 22 June 1976 (22.06.1976) col 13, ln 32 to col 14, ln 40; col 17, ln 13-35	1-2, 4-9
Y		3
Y	Venkatathri, Synthesis of high silica content silicoaluminophosphate-5 (SAPO-5) from non-aqueous medium using hexamethyleneimine template, Jornal of Scientific & Industrial Research, Vol 64, pp 509-514 (July 2005)	3
Y	Sinha et al., An improved method for the synthesis of the silicoaluminophosphate molecular sieves, SAPO-5, SAPO-11 and SAPO-31, Microporous and Mesoporous Materials 31, 321-331 (1999) abstract	1-9
Y	Martinez et al., Inorganic molecular sieves: Preparation, modification and industrial application in catalytic processes, Coordination Chemistry Reviews 255, 1558-1580 (2011) abstract, entire document	1-9
Y	US 2005/0209492 A1 (Ghosh et al.) 22 September 2005 (22.09.2005) para [0019]- [0038]	1-9
Y	US 4,529,828 A (Antos et al.) 16 July 1985 (16.07.1985) col 10, ln 16-67	1-9
Y	US 2002/0068844 A1 (William et al.) 06 June 2002 (06.06.2002) para [0039]- [0051]	1-9
Y	US 5,994,603 A (Mohr et al.) 30 November 1999 (30.11.1999) col 2, ln 38-59, col 4-10	1-9
Y	US 6,689,929 B2 (William et al.) 10 February 2004 (10.02.2004) col 8, ln 21 to col 9, ln 34	1-9

☒ Further documents are listed in the continuation of Box C.

* 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 application or patent 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

26 February 2014 (26.02.2014)

Date of mailing of the international search report

31 MAR 2014

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents
P.O. Box 1450, Alexandria, Virginia 22313-1450
Facsimile No. 571-273-3201

Authorized officer:

Lee W. Young

PCT Helpdesk: 571-272-4300
PCT OSP: 571-272-7774

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4,529,828 A (Antos et al.) 16 July 1985 (16.07.1985) col 10, ln 16-67	1-9
A	US 2010/0029467 A1 (Inui et al.) 04 February 2010 (04.02.2010) entire document	1-9
A	US 2012/116139 A1 (Inui et al.) 10 May 2012 (10.05.2012) entire document	1-9