(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
19 September 2019 (19.09.2019)

WIPO | PCT

(10) International Publication Number
WO 2019/177954 A4

(51) International Patent Classification:
B01J 29/40 (2006.01) *B01J 29/76* (2006.01)
B01J 29/44 (2006.01) *B01J 29/78* (2006.01)
B01J 29/46 (2006.01) *B01J 29/80* (2006.01)
B01J 29/70 (2006.01) *B01J 35/00* (2006.01)
B01J 29/74 (2006.01) *C01B 39/02* (2006.01)

(21) International Application Number:
PCT/US2019/021588

(22) International Filing Date:
11 March 2019 (11.03.2019)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
18382167.7 14 March 2018 (14.03.2018) EP

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(54) Title: METHODS OF PRODUCING COMPOSITE ZEOLITE CATALYSTS FOR HEAVY REFORMATE CONVERSION INTO XYLENES

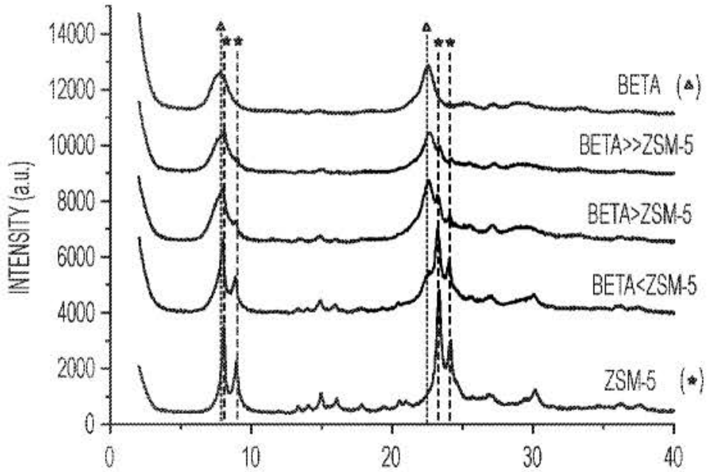

FIG. 1A

(57) Abstract: A method of forming a composite zeolite catalyst includes combining a silicon source and an aqueous organic structure directing agent having a polyamino cation compound to form a silica intermediary gel, introducing an aluminum precursor to the silica intermediary gel to form a catalyst precursor gel, evaporating water in the catalyst precursor gel to form a catalyst gel, and heating the catalyst gel to form a composite zeolite catalyst particle having an intergrowth region with a mixture of both Beta crystals and ZSM-5 crystals. An associated method of making xylene includes feeding heavy reformate to a reactor, the reactor containing the composite zeolite catalyst, and producing xylene by simultaneously performing dealkylation and transalkylation of the heavy reformate in the reactor, where each composite zeolite catalyst particle is able to catalyze both the dealkylation and transalkylation reactions.

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(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, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, 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, ST, 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).

Published:

— *with international search report (Art. 21(3))*

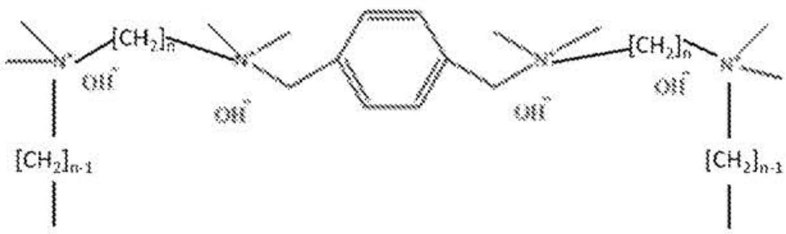
— *with amended claims (Art. 19(1))*

Date of publication of the amended claims:
14 November 2019 (14.11.2019)

AMENDED CLAIMS
received by the International Bureau on 18 October 2019 (18.10.2019)

1. A method of forming a composite zeolite catalyst, the method comprising:

combining a silicon source and an aqueous organic structure directing agent to form a silica intermediary gel, where the aqueous organic directing structure agent comprises a polyamino cation compound having a structure in accordance with



, with "n" varying in the range of 6 to 22;

introducing an aluminum precursor to the silica intermediary gel to form a catalyst precursor gel;

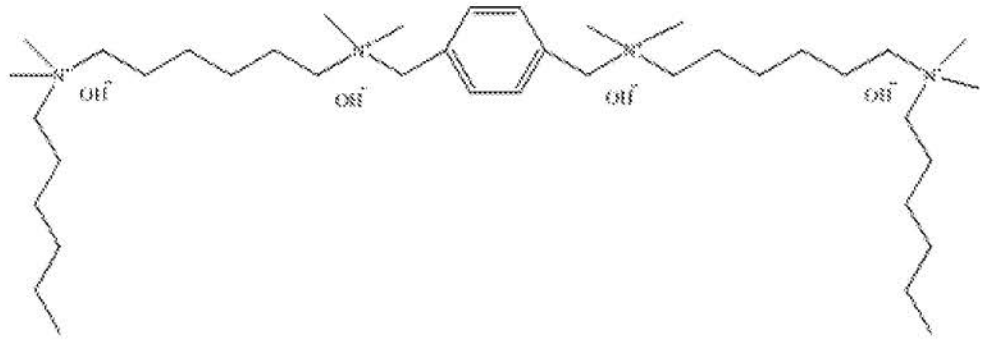
evaporating the water in the catalyst precursor gel to form a catalyst gel; and

heating the catalyst gel to form a composite zeolite catalyst particle, where the catalyst particle has both Beta and ZSM-5 zeolites and is characterized by having an intergrowth region with a mixture of both Beta crystals and ZSM-5 crystals.

2. The method of claim 1 where the silicon source comprises a silica gel, silicon oxide, silicon halide, tetraalkyl orthosilicate, silicate, silicic acid, fumed silica, sodium silicate, colloidal silica, or combinations thereof.

3. The method of claim 1 where the silicon source is a silica gel and the silica gel is a 20 to 60 wt. % suspension of silica in water.

4. The method of any preceding claim where the polyamino cation comprises a structure in accordance with:



5. The method of any preceding claim where the aqueous organic directing structure comprises from 5 to 15 wt. % polyamino cation and from 85 to 95 wt. % water.

6. The method of any preceding claim where the aluminum precursor is alumina (Al_2O_3), aluminum hydroxide ($Al(OH)_3$), aluminum oxide hydroxide ($AlO(OH)$), or combinations thereof.

7. The method of any preceding claim where the heating of the catalyst gel is conducted in a sealed vessel under autogenous pressure at a temperature from 130 to 180 °C with stirring and the heating is continued for 4-10 days.

8. The method of any preceding claim where the method further comprises impregnating the composite zeolite catalyst with up to 20 wt. % of one or more metals selected from the group consisting of molybdenum, chromium, platinum, nickel, tungsten, palladium, ruthenium, gold, rhenium, rhodium, or combinations thereof to yield impregnated composite zeolite catalyst.

9. A composite zeolite catalyst,

the composite zeolite catalyst comprises ZSM-5 and Beta within a single catalyst particle,

where the composite zeolite catalyst has an intergrowth region with a mixture of Beta crystals and ZSM-5 crystals, the intergrowth of ZSM-5 and Beta characterized by an XRD curve having signature peaks at 7.6±0.2, 7.9±0.2, 8.8±0.2, 22.4±0.2, 23.1±0.2 and 23.9±0.2, and where

the composite zeolite catalyst further comprises up to 20 wt. % of one or more metals selected from the group consisting of molybdenum, tungsten, ruthenium, gold, rhenium, rhodium, or combinations thereof to yield impregnated zeolite catalyst.

10. The composite zeolite catalyst of claim 9, where the composite zeolite catalyst further comprises up to 20 wt. % rhenium in the form of ammonium perrhenate, molybdenum in the form of ammonium molybdate tetrahydrate, or combinations thereof to yield impregnated zeolite catalyst.

11. A method of making xylene, the method comprising:

feeding heavy reformate to a reactor, the reactor containing a composite zeolite catalyst comprising a plurality of catalyst particles, where each catalyst particle comprises both ZSM-5 and Beta zeolites and has an intergrowth region with a mixture of both Beta crystals and ZSM-5 crystals; and

producing xylene by simultaneously performing transalkylation and dealkylation of the heavy reformate in the reactor, where each composite zeolite catalyst particle is able to simultaneously catalyze both the transalkylation and dealkylation reactions,

where the composite zeolite catalyst further comprises up to 20 wt. % of one or more metals selected from the group consisting of molybdenum, tungsten, ruthenium, gold, rhenium, rhodium, or combinations thereof to yield impregnated zeolite catalyst.

12. The method of claim 11, where the composite zeolite catalyst further comprises up to 20 wt. % rhenium in the form of ammonium perrhenate, molybdenum in the form of ammonium molybdate tetrahydrate, or combinations thereof to yield impregnated zeolite catalyst.

13. The method of claim 11 or 12, where the heavy reformate comprises at least 15 wt. % methylethylbenzene (MEB) and at least 50 wt. % trimethylbenzene (TMB).

14. A system for making xylene, the system comprising:

a reactor, the reactor containing a composite zeolite catalyst comprising a plurality of catalyst particles, where each catalyst particle comprises both ZSM-5 and Beta zeolites and has an intergrowth region with a mixture of both Beta crystals and ZSM-5 crystals, where

the composite zeolite catalyst further comprises up to 20 wt. % of one or more metals selected from the group consisting of molybdenum, tungsten, ruthenium, gold, rhenium, rhodium, or combinations thereof to yield impregnated composite zeolite catalyst.

15. The system of claim 14, where the composite zeolite catalyst further comprises up to 20 wt. % rhenium in the form of ammonium perrhenate, molybdenum in the form of ammonium molybdate tetrahydrate, or combinations thereof to yield impregnated zeolite catalyst.