diffusion resistance and high activity for the isomerization of xylenes while minimizing xylene loss to transmethylation reactions.

BRIEF SUMMARY

The present disclosure provides boroaluminosilicate molecular sieves for use as xylene isomerization catalysts. Such boroaluminosilicate molecular sieves have surprisingly been found to exhibit unexpectedly high xylene isomerization activity while simultaneously yielding less transmethylation byproducts (C_7 and C_9 aromatics) compared to industry standard catalysts. Also provided are methods for use of these boroaluminosilicate molecular sieves for enriching the p-xylene content of a hydrocarbon-containing feed stream comprising xylene isomers. Such catalysts include boroaluminosilicate molecular sieves that can be prepared, for example, in substantially H^+-form through the use of an organic base, eliminating the need for a cation exchange step to remove alkali metal which can degrade isomerization performance.

In one aspect, the disclosure provides a boroaluminosilicate molecular sieve having an average crystallite size less than 2 μm, wherein the alkali metal content is less than 400 ppmw.

Accordingly, in one embodiment, the disclosure provides the hydrogen form of boroaluminosilicate molecular sieves having an average crystallite size less than 2 μm.

In another aspect, the disclosure provides a method for increasing the proportion of p-xylene (pX) in a hydrocarbon-containing feed stream comprising xylene isomers, said method comprising contacting the hydrocarbon-containing feed stream with an isomerization catalyst described herein and under conditions suitable to yield a stream enriched in p-xylene with respect to the hydrocarbon-containing feed stream.

In another aspect, the disclosure provides a method of increasing the proportion of p-xylene (pX) in a hydrocarbon-containing feed stream comprising xylene isomers, said method comprising: contacting the hydrocarbon-containing feed stream with an isomerization catalyst under conditions suitable to yield a stream enriched in p-xylene with respect to the hydrocarbon-containing feed stream, wherein the isomerization catalyst comprises a boroaluminosilicate molecular sieve prepared using an amine base, wherein the boroaluminosilicate molecular sieve has an alkali metal content less than 400 ppmw and wherein the boroaluminosilicate molecular sieve has an average crystallite size less than 2 μm. In an embodiment, the disclosure relates to a method for increasing the proportion of p-xylene (pX) in a hydrocarbon-containing feed stream comprising xylene isomers, said method comprising contacting the hydrocarbon-containing feed stream with an isomerization

catalyst under conditions suitable to yield a stream enriched in p-xylene with respect to the hydrocarbon-containing feed stream, wherein the isomerization catalyst comprises a boroaluminosilicate molecular sieve prepared using an amine base.

In another aspect, the disclosure provides a catalyst system for enriching a mixed xylenes feed in p-xylene comprising a first bed comprising an ethylbenzene (EB) conversion catalyst and a second bed comprising an isomerization catalyst that comprises a boroaluminosilicate molecular sieve, wherein the boroaluminosilicate molecular sieve has an alkali metal content less than 400 ppmw and wherein the boroaluminosilicate molecular sieve has an average crystallite size less than 2 μm. In an embodiment, the disclosure relates to a catalyst system for enriching a xylene isomers feed in p-xylene comprising a first bed comprising an ethylbenzene (EB) conversion catalyst and a second bed comprising an isomerization catalyst that comprises a boroaluminosilicate molecular sieve. In another aspect, the disclosure provides a xylene isomerization reactor having a reaction zone containing a catalyst system as described above.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1a is a flow diagram illustrating one illustrative embodiment of a method for xylene isomerization.

Figure 1b is a flow diagram illustrating another illustrative embodiment of a method for xylene isomerization.

Figure 1c is a flow diagram illustrating a third illustrative embodiment of a method for xylene isomerization.

We claim:

1. A boroaluminosilicate molecular sieve having an average crystallite size less than 2 μm, wherein the alkali metal content is less than 400 ppmw.

2. The boroaluminosilicate molecular sieve of claim 1, wherein the average crystallite size is between 50 nm to 1 μm.

~~3. The boroaluminosilicate molecular sieve of claim 1 or 2, wherein the alkali metal content is less than 400 ppmw.~~

43. The boroaluminosilicate molecular sieve of claim 1~~, 2,~~ or ~~3~~2, wherein the alkali metal content is less than 150 ppmw.

~~5~~4. A method of increasing the proportion of p-xylene (pX) in a hydrocarbon-containing feed stream comprising xylene isomers, said method comprising:

contacting the hydrocarbon-containing feed stream with an isomerization catalyst according to any one of claims 1-43 and under conditions suitable to yield a stream enriched in p-xylene with respect to the hydrocarbon-containing feed stream.

~~6~~5. A method of increasing the proportion of p-xylene (pX) in a hydrocarbon-containing feed stream comprising xylene isomers, said method comprising:

contacting the hydrocarbon-containing feed stream with an isomerization catalyst under conditions suitable to yield a stream enriched in p-xylene with respect to the hydrocarbon-containing feed stream, wherein

the isomerization catalyst comprises a boroaluminosilicate molecular sieve prepared using an amine base, wherein the boroaluminosilicate molecular sieve has an alkali metal content less than 400 ppmw and wherein the boroaluminosilicate molecular sieve has an average crystallite size less than 2 μm.

~~7~~6. The method of claim ~~6~~5, wherein the boroaluminosilicate molecular sieve is prepared using ethylenediamine.

~~8. The method of claim 6 or 7, wherein the boroaluminosilicate molecular sieve has an alkali metal content is less than 400 ppmw.~~

97. The method of any one of claims 54-86, further comprising recovering byproducts from the pX enriched stream.

108. The method of any one of claims 54-97, wherein the byproducts contain 1.5 wt. % or less net toluene byproduct.

119. The method of any one of claims 54-108, wherein the byproducts contain 3.5 wt. % or less net C_9-byproducts.

1210. The method of any one of claims 54-119, wherein the pX enriched stream contains less than 0.7 wt. % net trimethylbenzene byproduct.

1311. The method of any one of claims 54-1210, wherein the pX enriched stream contains less than 1.0 wt.% net toluene.

1412. The method of any one of claims 54-1311, wherein the pX enriched stream contains less than 0.5 wt. % net trimethylbenzene byproduct.

1513. The method of any one of claims 54-1412, wherein the pX enriched stream contains at least 23.5 wt.% pX/X and less than 1.5 wt.% net toluene byproduct.

1614. The method of any one of claims 54-1412, wherein the pX enriched stream contains at least 23.5 wt.% pX/X and less than 1.0 wt.% net trimethylbenzene byproduct.

1715. The method of any one of claims 54-1412, wherein

the pX enriched stream contains at least 23.5 wt.% pX/X and a ratio of pX/X to the sum of net wt.% trimethylbenzene byproduct and net wt.% toluene byproduct of greater than 4.0.

1816. The method of any one of claims 54-1715, wherein the hydrocarbon-containing feed stream comprises at least 80 wt. % xylene isomers and pX/X of less than 12 wt.%.

1917. The method of any one of claims 54-1816, wherein the hydrocarbon-containing feed stream is contacted with the isomerization catalyst in the presence of hydrogen.

2018. The method of any one of claims 54-1917, further comprising recovering a pX product from the pX enriched stream, thereby forming a pX-lean stream.

2119. The method of claim 2018, wherein the pX-lean stream is recycled for use as the hydrocarbon-containing feed stream.

2220. The method of any one of claims 54-2119, further comprising forming a combination stream by combining a make-up feed stream comprising xylene isomers with the pX enriched stream.

2321. The method of claim 2119, further comprising recovering a pX product from the combination stream, thereby forming a pX-lean stream for use as a hydrocarbon-containing feed stream.

2422. The method of any one of claims 2220-2321, further comprising recovering byproducts from the combination stream.

2523. The method of any one of claims 54-2422, further comprising contacting the hydrocarbon-containing feed stream with an ethylbenzene (EB) conversion catalyst under conditions suitable to reduce the EB content of the hydrocarbon-containing feed stream.

2624. The method of claim 2523, wherein the hydrocarbon-containing feed stream is contacted with the EB conversion catalyst prior to being contacted with the isomerization catalyst.

2725. The method of claim 2523; wherein the hydrocarbon-containing feed stream is contacted with the EB conversion catalyst and the isomerization catalyst in a single reaction zone.

2826. The method of any one of claims 2523-2725, wherein the EB conversion catalyst comprises an AI-MFI molecular sieve or a ZSM-5-type molecular sieve.

2927. The method of any one of claims 54-2826, wherein the isomerization catalyst further comprises a support.

3028. The method of claim 2927, wherein the support comprises alumina, silica, titania, or a mixture thereof.

3129. The method of claim 3028, wherein the support comprises silica.

3230. The method of claim 3028, wherein the support comprises titania.

~~33~~31. The method of claim ~~30~~28, wherein the support comprises alumina.

~~34~~32. The method of claim ~~33~~31, wherein the support comprises a mixture of alumina and silica.

~~35~~33. A catalyst system for enriching a mixed xylenes feed in p-xylene comprising

a first bed comprising an ethylbenzene (EB) conversion catalyst and a second bed comprising an isomerization catalyst that comprises a boroaluminosilicate molecular sieve, wherein the boroaluminosilicate molecular sieve has an alkali metal content less than 400 ppmw and wherein the boroaluminosilicate molecular sieve has an average crystallite size less than 2 μm.

~~36. The catalyst system of claim 35, wherein the boroaluminosilicate molecular sieve has an alkali metal content less than 400 ppmw.~~

~~37. The catalyst system of claim 35 or 36, wherein the boroaluminosilicate molecular sieve has an average crystallite size less than 2 μm.~~

~~38~~34. The catalyst system of claim ~~35~~ 33~~or 36~~, wherein the boroaluminosilicate molecular sieve has an average crystallite size between 50 nm to 1 μm.

~~39~~35. The catalyst system of ~~any one of~~ claim~~s~~ ~~35~~33 ~~or~~ ~~38~~34, wherein the boroaluminosilicate molecular sieve is prepared using a base.

~~40~~36. The catalyst system of claim ~~39~~35, wherein the isomerization catalyst is prepared by:

combining a boron source, an aluminum source, a silica sol, and a template with the base to form a reaction mixture;

warming the reaction mixture to provide a product mixture comprising a solid;

isolating the solid from the product mixture; and

calcining the solid to yield the isomerization catalyst.

~~41~~37. The catalyst system of claim ~~40~~36, wherein the template is tetrapropylammonium bromide or tetrapropylammonium hydroxide.

~~42~~38. The catalyst system of any one of claims ~~39~~35-~~41~~37, wherein the base comprises ethylenediamine.

4339. The catalyst system of any one of claims 3533-4238, wherein the EB conversion catalyst comprises an AI-MFI molecular sieve or a ZSM-5-type molecular sieve.

4440. The catalyst system of any one of claims 3533-4339, wherein the isomerization catalyst further comprises a support.

4541. The catalyst system of claim 4440, wherein the support comprises alumina, silica, titania, or a mixture thereof.

4642. The catalyst system of claim 4541, wherein the support comprises silica.

4743. The catalyst system of claim 4541, wherein the support comprises titania.

4844. The catalyst system of claim 4541, wherein the support comprises alumina.

4945. The catalyst system of claim 4541, wherein the support comprises a mixture of alumina and silica.

5046. The catalyst system of any one of claims 3533-4945, wherein the first bed is disposed over the second bed.

5147. The catalyst system of claim 5046, wherein a guard bed comprising a hydrogenation catalyst component is disposed over the first bed.

5248. The catalyst system of claim 5046, wherein a guard bed comprising a hydrogenation catalyst component is disposed between the first bed and the second bed.

5349. A xylene isomerization reactor comprising a reaction zone containing a catalyst system of any one of claims 3533-5248.

5450. The method of any of claims 54-3432, wherein the isomerization catalyst further comprises a hydrogenation catalyst component.

5551. The catalyst system of any of claims 3533-5046, further comprising a hydrogenation catalyst component.

5652. The method of any of claims 54-3432 and 5450, wherein the isomerization catalyst has an aluminum content of 0.01 wt% to 3.3 wt%.

5753. The method of any of claims 54-3432, 50 and 54-5652, wherein the isomerization catalyst has a boron content of 0.01wt% to 2.0wt%.

5854. The catalyst system of any of claims 3533-5046 and 5551, wherein the isomerization catalyst has an aluminum content of 0.01 wt% to 3.3 wt%.

5955. The catalyst system of any of claims 3533-5046, 5551, and 5854, wherein the isomerization catalyst has a boron content of 0.01wt% to 2.0wt%.