

SELECTIVE OLIGOMERIZATION OF ISOBUTENE

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of prior U.S. provisional application Serial no.
5 60/982,984 filed October 26, 2007 which is hereby incorporated by reference in its entirety.

FIELD

[0002] The present invention relates to the selective oligomerization of isobutene.

BACKGROUND

[0003] The selective oligomerization of isobutene is an important chemical reaction,
10 particularly where the isobutene is contained in a refinery C₄ hydrocarbon stream, such as Raffinate-1 and Raffinate-2.

[0004] For example, C₄ linear olefins are an attractive feedstock for producing octenes with zeolite catalysts because, among other reasons, the resulting octenes have triple branching of less than about 5 wt %. However, when isobutene is present in significant
15 quantities (> 10 wt%) in the oligomerization feedstock, such as with Raffinate-1, the amount of triple-branched octenes increases to a level which is unacceptable for some end uses such as certain plasticizers. In the past, this problem was generally addressed by selectively reacting the isobutene with methanol to produce methyl t-butyl ether (MTBE). However, with the phase-out of MTBE because of environmental concerns, this reaction is no longer an
20 attractive method of removing isobutene. As a result, interest has focused on selective dimerization of the isobutene to produce octenes useful as, for example, gasoline octane enhancers and as feedstocks for producing C₉ aldehydes and/or alcohols.

[0005] Another use for the selective oligomerization of isobutene is in the purification of C₄ olefin streams used in the alkylation of benzene to produce sec-butylbenzene, an important
25 precursor in the production of phenol. Thus, even when present at only low levels (< 5 wt%) in a C₄ olefin stream, such as Raffinate-2, isobutene reacts with benzene to produce tert-butylbenzene. However, tert-butylbenzene is difficult to separate from sec-butylbenzene by distillation since the boiling points of the two butylbenzene isomers are very similar, 169°C for tert-butylbenzene as compared with 173°C for sec-butylbenzene. Moreover, tert-
30 butylbenzene is known to be an inhibitor to the oxidation of sec-butylbenzene to the corresponding hydroperoxide, which is the first step in the conversion of sec-butylbenzene to phenol and methyl ethyl ketone.

[0006] One example of a process for the dimerization of isobutene is disclosed in U.S. Patent No. 6,914,166, in which a C₄ olefinic feedstock containing isobutene and n-butene(s) is contacted with dealuminated zeolite beta under conditions including a temperature below 50°C effective to allow selective dimerization of isobutene to trimethylpentene(s). However, although this process appears to be highly selective for isobutene conversion, the catalyst is found to age rapidly at the conditions employed.

[0007] U.S. Patent No. 6,274,783 discloses a process for the concurrent dimerization and hydrogenation of isobutene in a single distillation column reactor containing both a dimerization catalyst, such as a zeolite or an acidic cation exchange resin, and a hydrogenation catalyst, such as a Group VIII metal deposited on a carrier or support. There is no indication that the process would selectively dimerize isobutene in a mixed C₄ olefin feed.

[0008] U.S. Patent No. 6,500,999 discloses a process for the production of hydrocarbons with a high octane number starting from hydrocarbon cuts containing isobutene by means of selective dimerization with acid catalysts, wherein the dimerization reaction is carried out in a tubular reactor using a feed containing isobutene in quantities of less than 20% by weight and with a molar ratio of linear olefins/isobutene greater than 3, preferably operating at a reaction temperature ranging from 30 to 120°C, at a pressure of less than 5 MPa and at feed space velocities of less than 60 hr⁻¹. Suitable acid catalysts are said to include phosphoric acid supported on a solid carrier, a cationic acid exchange resin, a liquid acid, a sulfonic acid derivative, a silico-alumina, a mixed oxide, a zeolite or a fluorinated or chlorinated alumina.

[0009] U.S. Patent No. 7,112,711 discloses a process for oligomerizing alkenes having from 3 to 6 carbon atoms, including isobutene, in the presence of a catalyst containing a zeolite of the MFS structure type. The process is carried out at a temperature comprised between 125 and 175°C when the feedstock contains only alkenes with 3 carbon atoms and between 140 and 240°C when the feedstock contains at least one alkene with 4 or more carbon atoms

[0010] U.S. Patent Application Publication No. 2007/0213576, published September 13, 2007, discloses a process for the dimerization of isobutene at a temperature in excess of 240°C in the presence of a multi-dimensional molecular sieve catalyst containing at least one 10 or 12 ring channel, such as ZSM-57, ZSM-5, FAU, Beta, ZSM-12, mordenite, MCM-22 family zeolites, and mixtures thereof to produce a product low in triple-branched octenes.

[0011] K. Hauge et al in *Catalysis Today*, Vol. 100 (2005) pp. 463-466 reported on the oligomerization of pure isobutene over solid acid catalysts at 40°C and 10 bar pressure and 60 WHSV. The zeolite solid acid catalysts (ZSM-5, beta, and Y) had high initial activity, but the activity dropped drastically over the course of 2 hours. This was attributed to “the
5 production of high molecular weight oligomers inside the zeolite pores.” The macroreticular acidic resin Amberlyst 15, in contrast, showed activity that leveled out after about 2 hours.

[0012] According to the present invention, it has now been found that, when operated at low temperature, molecular sieves of the MCM-22 family are selective and stable catalysts for the oligomerization of isobutene in the presence of other C₄ alkenes. Although the reason
10 for this result is not understood, it is believed that the presence of the active acid sites in pockets on the external surface of the zeolite crystal in MCM-22 molecular sieves allows the reaction products to quickly desorb, thereby avoiding the production of high molecular weight oligomers inside the zeolite pores as reported by K. Hauge et al in *Catalysis Today*, Vol. 100.

15 SUMMARY

[0013] In one aspect, the invention resides in a process for oligomerizing isobutene, the process comprising contacting a feedstock comprising isobutene with a catalyst comprising a MCM-22 family molecular sieve under conditions effective to oligomerize said isobutene, said conditions including a temperature from about 45°C to less than 140°C.

20 [0014] Conveniently, said conditions include a temperature from about 50°C to about 120°C and/or a pressure of from about 345 to 1379 kPag (about 50 to about 2000 psig).

[0015] Conveniently, the molecular sieve has an X-ray diffraction pattern including d-spacing maxima at 12.4±0.25, 6.9±0.15, 3.57±0.07 and 3.42±0.07 Angstrom. Generally, the molecular sieve is selected from MCM-22, PSH-3, SSZ-25, ERB-1, ITQ-1, ITQ-2, MCM-36,
25 MCM-49, MCM-56, UZM-8, and combinations of any two or more thereof, especially from MCM-22, MCM-49, MCM-56 and combinations of any two or more thereof.

[0016] In one embodiment, the feedstock also comprises at least one additional C₄ alkene, such as n-butene.

30 [0017] In a further aspect, the invention resides in a process for producing sec-butylbenzene, the process comprising:

(a) contacting a C₄ hydrocarbon feedstock comprising isobutene and at least one n-butene with a catalyst comprising a MCM-22 family molecular sieve under conditions effective to selectively oligomerize the isobutene, said conditions including a temperature

from about 45°C to less than 140°C and said contacting producing an effluent comprising isobutene oligomers and said at least one n-butene;

(b) separating said at least one n-butene from the effluent;

(c) contacting said at least one n-butene separated in (b) with benzene under
5 alkylation conditions and in the presence of an alkylation catalyst to produce sec-butylbenzene.

[0018] In one embodiment, said C₄ hydrocarbon feedstock comprises up to 5 wt% isobutene for example from 2 to 5 wt%, such as from 3 to 5 wt% isobutene. Preferably the conditions are selected such that the effluent contains less than 0.3 wt% isobutene, such as
10 less than 0.2 wt% isobutene, for example from 0.01 to 0.2 wt % isobutene. In a further embodiment, said C₄ hydrocarbon feedstock comprises at least 90 wt% of n-butenes and the conditions and catalyst are selected such that said contacting (a) oligomerizes no more than 12 wt% of said n-butenes.

[0019] Conveniently, the process further comprises (d) contacting the effluent with water
15 and/or an alcohol prior to said separating (b), said contacting (d) converting at least part of any isobutene remaining in the effluent to an ether.

[0020] In one embodiment, the alkylation catalyst comprises a MCM-22 family molecular sieve.

[0021] Conveniently, the process further comprises:

20 (e) oxidizing the sec-butylbenzene from (c) to produce a hydroperoxide; and
(f) cleaving the hydroperoxide from (e) to produce phenol and methyl ethyl ketone.

BRIEF DESCRIPTION OF THE DRAWINGS

[0022] Figure 1 is a graph of product isobutene concentration against temperature in the
25 butene oligomerization process of Example 1.

[0023] Figure 2 is a graph of n-butene conversion against product isobutene concentration in the butene oligomerization process of Example 1.

DETAILED DESCRIPTION

[0024] Described herein is a process for oligomerizing isobutene in a feedstock wherein
30 the feedstock is contacted with a catalyst comprising a MCM-22 family molecular sieve under conditions, including a temperature from about 45°C to less than 140°C, effective to oligomerize the isobutene and produce an effluent containing less isobutene than in the feedstock.

[0025] The feedstock can be any process stream containing isobutene, including a pure isobutene stream. In general, however, the feedstock is an olefinic C₄ hydrocarbon mixture containing isobutene and at least one linear butene, namely butene-1, cis- butene-2, trans-butene-2 or mixtures thereof. Such olefinic C₄ hydrocarbon mixtures can be obtained by steam cracking of ethane, propane, butane, LPG and light naphthas; catalytic cracking of naphthas and other refinery feedstocks; and by conversion of oxygenates, such as methanol, to lower olefins. The present oligomerization process then serves to reduce the isobutene concentration of the olefinic C₄ hydrocarbon mixture.

[0026] For example, the following olefinic C₄ hydrocarbon mixtures are generally available in any refinery employing steam cracking to produce olefins: a crude steam cracked butene stream, Raffinate-1 (the product remaining after solvent extraction or hydrogenation to remove butadiene from a crude steam cracked butene stream) and Raffinate-2 (the product remaining after removal of butadiene and isobutene from a crude steam cracked butene stream). Generally, these streams have compositions within the weight ranges indicated in Table 1 below.

Table 1

Component	Crude C ₄ stream	Raffinate 1		Raffinate 2	
		Solvent Extraction	Hydrogenation	Solvent Extraction	Hydrogenation
Butadiene	30-85%	0-2%	0-2%	0-1%	0-1%
C ₄ acetylenes	0-15%	0-0.5%	0-0.5%	0-0.5%	0-0.5%
Butene-1	1-30%	20-50%	50-95%	25-75%	75-95%
Butene-2	1-15%	10-30%	0-20%	15-40%	0-20%
Isobutene	0-30%	0-55%	0-35%	0-5%	0-5%
N-butane	0-10%	0-55%	0-10%	0-55%	0-10%
Iso-butane	0-1%	0-1%	0-1%	0-2%	0-2%

[0027] Other refinery mixed C₄ streams, such as those obtained by catalytic cracking of naphthas and other refinery feedstocks, typically have the following composition:

	Propylene	= 0-2 wt%
	Propane	= 0-2 wt%
	Butadiene	= 0-5 wt%
	Butene-1	= 5-20 wt%
5	Butene-2	= 10-50 wt%
	Isobutene	= 5-25 wt%
	Iso-butane	= 10-45 wt%
	N-butane	= 5-25 wt%

[0028] C₄ hydrocarbon fractions obtained from the conversion of oxygenates, such as methanol, to lower olefins more typically have the following composition:

	Propylene	= 0-1 wt%
	Propane	= 0-0.5 wt%
	Butadiene	= 0-1 wt%
	Butene-1	= 10-40 wt%
15	Butene-2	= 50-85 wt%
	Isobutene	= 0-10 wt%
	N- + iso-butane	= 0-10 wt%

[0029] Any one or any mixture of the above C₄ hydrocarbon mixtures can be used in the present isobutene oligomerization process.

[0030] In addition to other hydrocarbon components, commercial C₄ hydrocarbon mixtures typically contain other impurities which could be detrimental to the present oligomerization process or to use of the hydrocarbon mixture downstream of the present oligomerization process. For example, refinery C₄ hydrocarbon streams typically contain nitrogen and sulfur impurities, whereas C₄ hydrocarbon streams obtained by oxygenate conversion processes typically contain unreacted oxygenates and water. Thus, prior to the present oligomerization step, these mixtures may also be subjected to one or more of sulfur removal, nitrogen removal and oxygenate removal. Removal of sulfur and/or nitrogen and/or oxygenate impurities is conveniently effected by one or a combination of any of caustic treatment, water washing, distillation, adsorption using molecular sieves and membrane separation. Water is also typically removed by adsorption.

[0031] Conveniently, the feed to the present oligomerization process contains, by weight, less than 1000 ppm, such as less than 500 ppm, for example less than 100 ppm, water. Typically, the feed contains less than 100 ppm, such as less than 30 ppm, for example less than 3 ppm, sulfur. Conveniently, the feed contains less than 10 ppm, such as less than 1 ppm, for example less than 0.1 ppm, nitrogen. Ideally, the feed contains less than 1000 ppm water and less than 100 ppm sulfur and less than 10 ppm nitrogen, such as less than 500 ppm,

30 ppm, 1 ppm water, sulfur, nitrogen respectively, most preferably less than 100 ppm, 3 ppm, 0.1 ppm water, sulfur, nitrogen respectively.

[0032] The oligomerization catalyst employed in the present process is at least one molecular sieve of the MCM-22 family. As used herein, the term "MCM-22 family material" (or "material of the MCM-22 family" or "molecular sieve of the MCM-22 family" or "MCM-22 family zeolite"), includes one or more of:

- molecular sieves made from a common first degree crystalline building block unit cell, which unit cell has the MWW framework topology. (A unit cell is a spatial arrangement of atoms which if tiled in three-dimensional space describes the crystal structure. Such crystal structures are discussed in the "Atlas of Zeolite Framework Types", Fifth edition, 2001, the entire content of which is incorporated as reference);
- molecular sieves made from a common second degree building block, being a 2-dimensional tiling of such MWW framework topology unit cells, forming a monolayer of one unit cell thickness, preferably one c-unit cell thickness;
- molecular sieves made from common second degree building blocks, being layers of one or more than one unit cell thickness, wherein the layer of more than one unit cell thickness is made from stacking, packing, or binding at least two monolayers of one unit cell thickness. The stacking of such second degree building blocks can be in a regular fashion, an irregular fashion, a random fashion, or any combination thereof; and
- molecular sieves made by any regular or random 2-dimensional or 3-dimensional combination of unit cells having the MWW framework topology.

[0033] Molecular sieves of the MCM-22 family include those molecular sieves having an X-ray diffraction pattern including d-spacing maxima at 12.4 ± 0.25 , 6.9 ± 0.15 , 3.57 ± 0.07 and 3.42 ± 0.07 Angstrom. The X-ray diffraction data used to characterize the material are obtained by standard techniques such as using the K-alpha doublet of copper as incident radiation and a diffractometer equipped with a scintillation counter and associated computer as the collection system.

[0034] Materials of the MCM-22 family include MCM-22 (described in U.S. Patent No. 4,954,325), PSH-3 (described in U.S. Patent No. 4,439,409), SSZ-25 (described in U.S. Patent No. 4,826,667), ERB-1 (described in European Patent No. 0293032), ITQ-1 (described in U.S. Patent No. 6,077,498), ITQ-2 (described in International Patent Publication No. WO97/17290), MCM-36 (described in U.S. Patent No. 5,250,277), MCM-49 (described in U.S. Patent No. 5,236,575), MCM-56 (described in U.S. Patent No. 5,362,697), UZM-8

(described in U.S. Patent No. 6,756,030), and mixtures thereof. Generally, the molecular sieve is selected from (a) MCM-49, (b) MCM-56 and (c) isotypes of MCM-49 and MCM-56, such as ITQ-2.

5 **[0035]** The MCM-22 family molecular sieve can be used in the present process in unbound (neat) form, or can be combined with a conventional metal oxide binder, such as alumina.

10 **[0036]** The present oligomerization process is conducted at a relatively low temperature of from about 45°C to less than 140°C, such as from about 50°C to about 120°C. The pressure employed in the process is not closely controlled, but generally will be between about 345 and about 13790 kPag (about 50 and about 2000 psig), typically between about 1379 and about 5516 kPag (about 200 and about 800 psig), such that at least the butenes are substantially in the liquid phase during the oligomerization process. The process can be conducted as a continuous or a batch process, and in the case of the more preferred continuous process, the butene feed is preferably contacted with the catalyst at a LHSV of
15 about 4 to about 16. In addition, the process can be conducted in any suitable reaction zone such as, for example, in a flow reactor containing a fixed catalyst bed or in a catalytic distillation reactor. Staged reaction in a number of series-connected reaction zones is also contemplated.

20 **[0037]** The present process selectively converts isobutene in an olefinic C₄ hydrocarbon mixture to heavier products, mainly branched C₈ and C₁₂ oligomers, which can readily be separated from the product effluent by distillation. Of course, in the case of catalytic distillation, reaction and separation may occur simultaneously. After separation, the oligomers, eg the C₈ and C₁₂ oligomers can be hydrogenated and used for fuel or other applications, including solvents. The remaining iso-butene deficient C₄ hydrocarbon mixture can
25 then be used as a feed, for example, in the production of sec-butylbenzene.

30 **[0038]** Although the MCM-22 family zeolites employed in the present oligomerization process are highly resistant to the aging problems reported with other zeolitic materials, such as zeolite beta, in practice the catalyst will tend to slowly lose activity and require rejuvenation and/or regeneration. The catalyst may be rejuvenated by treatment in an inert liquid (such as a non-olefinic hydrocarbon), and may be regenerated by contacting at elevated temperature with an oxygen-containing gas.

[0039] The oligomerization process described herein employing MCM-22 family molecular sieves as a catalyst is effective in selectively removing isobutene from

hydrocarbon feedstocks comprising isobutene and at least one additional C₄ alkene. In particular, the process is effective in reducing the isobutene content of a stream containing up to 5 wt% isobutene, such as Raffinate-2, to less than 0.3 wt%, such as to less than 0.2 wt%, even to less than 0.15 wt%. Moreover, even with a feedstock containing at least 90 wt% of n-butenes, the present process oligomerizes no more than 12 wt% of said n-butenes. The resultant isobutene-deficient effluent can then be used as a feedstock for, for example, a linear butene oligomerization process to produce higher (C₈+) olefins or for the alkylation of benzene with linear butenes to produce sec-butylbenzene.

[0040] The alkylation of benzene with linear butenes using a MCM-22 family molecular sieve as the catalyst is described in International Patent Publication No. WO06/015826, the entire contents of which are incorporated herein by reference. In particular, it is found that, by using the present oligomerization process to reduce the isobutene content of a butene-containing feedstock, such as Raffinate-2, to less than 0.2 wt%, the resultant feed can be used to alkylate benzene with a high selectivity to sec-butylbenzene. Moreover, the amounts of tert-butylbenzene and butene oligomers produced during the alkylation step are reduced to very low levels. The resultant sec-butylbenzene product can then be converted to phenol and methyl ethyl ketone by oxidizing the sec-butylbenzene to produce sec-butylbenzene hydroperoxide and then cleaving the hydroperoxide. It is an advantage of the invention that the catalyst employed for the selective oligomerization of the isobutene can also be employed, under alkylation conditions, to alkylate benzene using the effluent from the oligomerization reaction.

[0041] The invention will now be more particularly described with reference to the Examples.

Example 1. Selective Isobutene Dimerization with MCM-22 Catalyst

[0042] A fresh MCM-22 catalyst with a nominal weight composition of 65% MCM-22 crystal and 35% Versal 300 alumina was used for the experiment. The catalyst was made by extruding the MCM-22 crystal with Versal 300 alumina into 1.6 mm (1/16 inch) diameter cylindrical extrudate. The extrudate was cut to 1.3 mm (1/20 inch) length and 0.25 g (0.5 cc) of this sized catalyst was used. The catalyst was diluted with sand to 3 cc and loaded into an isothermal, down-flow, fixed-bed, tubular reactor having an outside diameter of 4.76 mm (3/16 inch). The catalyst was dried at 260°C and 1 atm for 2 hours with 100 cc/min flowing nitrogen. Nitrogen was turned off and the reactor was cooled to 69°C. Mixed butenes (see

Table 1 for feed composition) was introduced into the reactor at 60 cc/hr until reactor pressure reached 3448 kPag (500 psig). Butene flow was then reduced to 6.0 cc/hr (12 LHSV). The product composition was analyzed online every 4 hours by an HP GC equipped with two parallel columns, a 60M BD-1 column and a 50M PLOT column. Liquid samples were collected daily to ensure material closure. Data were collected at 3448 kPag (500 psig) with temperature set at 69, 76, 83, and 90°C respectively. Representative data are shown in Table 2.

Table 2

Sample ID	Feed				
Days on Stream		16.7	18.5	19.7	23.0
Temperature, °C		69	76	83	90
<u>Composition, wt%</u>					
Isobutane	0.002	0.012	0.012	0.013	0.012
n-Butane	0.094	0.096	0.096	0.096	0.096
t-Butene	41.285	40.610	40.527	40.575	40.522
1-Butene	0.092	0.098	0.104	0.164	0.223
Isobutene	4.538	0.316	0.184	0.119	0.081
c-Butene	53.428	48.942	48.708	48.396	47.886
Butadiene	0.477	0.433	0.409	0.381	0.343
C ₅ - C ₇	0.083	0.195	0.199	0.199	0.201
C ₈ ⁼	0.000	7.621	8.200	8.515	9.018
C ₉ ⁺	0.000	1.675	1.559	1.540	1.615
Sum	100.0	100.0	100.0	100.0	100.0
<u>Conversion %</u>					
Isobutene		93.0	95.9	97.4	98.2
Butadiene		9.2	14.3	20.1	28.1
n-Butenes		5.4	5.8	6.0	6.5
<u>Selectivity, wt%</u>					
C ₅ - C ₇		1.18	1.17	1.14	1.09
C ₈ ⁼		81.01	83.04	83.72	83.88
C ₉ ⁺		17.81	15.79	15.14	15.02
Sum		100.0	100.0	100.0	100.0

[0043] The flow was then reduced to 3.6 cc/hr (7.2 LHSV) and more data were collected at 3448 kPag (500 psig) with temperature set at 90, 83, 76, and 69 respectively. Representative data are shown in Table 3.

Table 3

Sample ID	Feed				
Days on Stream		27.9	26.9	26.0	25.0
Temperature, °C		69	76	83	90
<u>Composition, wt%</u>					
Isobutane	0.002	0.012	0.015	0.014	0.012
n-Butane	0.094	0.096	0.099	0.095	0.096
t-Butene	41.285	40.570	40.516	40.461	40.305
1-Butene	0.092	0.105	0.144	0.214	0.325
Isobutene	4.538	0.139	0.076	0.042	0.021
c-Butene	53.428	48.935	48.521	47.867	46.849
Butadiene	0.477	0.425	0.396	0.344	0.283
C ₅ - C ₇	0.083	0.181	0.192	0.191	0.201
C ₈ ⁼	0.000	7.935	8.391	9.003	9.758
C ₉ ⁺	0.000	1.600	1.649	1.765	2.149
Sum	100.0	100.0	100.0	100.0	100.0
<u>Conversion %</u>					
Isobutene		96.93	98.34	99.07	99.54
Butadiene		10.83	16.93	27.83	40.58
n-Butenes		5.48	5.93	6.61	7.73
<u>Selectivity, wt%</u>					
C ₅ - C ₇		1.01	1.07	0.99	0.98
C ₈ ⁼		82.37	82.68	82.78	81.15
C ₉ ⁺		16.61	16.25	16.23	17.87
Sum		100.00	100.00	100.00	100.00

5 **[0044]** The data in Tables 1 and 2 show that MCM-22 is active and selective for converting isobutene to dimers or C₈⁼. The temperature required for the reaction was mild, in the range of 69-90°C. Very low levels of isobutene can be obtained by adjusting reaction temperature and/or flow rate.

10 **[0045]** The data are further shown in Figures 1 and 2. Figure 1 shows the effect of reaction temperature and feed flow rate on isobutene level. For example, to achieve an isobutene level of 0.07-0.08 wt% in the reactor effluent, the reactor could be operated at 76°C and 7.2 LHSV or at 90°C and 12 LHSV. To achieve an isobutene level of 0.12-0.14 wt% in the reactor effluent, the reactor could be operated at 69°C and 7.2 LHSV or at 83°C and 12 LHSV. Figure 2 shows the n-butene conversion as a function of isobutene level in the reactor effluent. For each mole of isobutene converted, about 1 mole of n-butene was also converted.

15 n-Butene conversion increased to a higher level as expected when the target isobutene level is very low.

Example 2: Sec-Butylbenzene Production Using MCM-22 Catalyst and 2-Butene Feed

[0046] A 1.0 gram sample of the same MCM-22 catalyst (65 % MCM-22/35% alumina binder) as used in Example 1 was used for the alkylation of benzene with 2-butene. The catalyst was in the form of a 1.6 mm (1/16inch) diameter cylindrical extrudate, chopped to 1.6 mm (1/16inch) length, and was diluted with sand to 3 cc and loaded into an isothermal, down-flow, fixed-bed, tubular reactor having an outside diameter of 4.76mm (3/16inch). The catalyst was dried at 150°C and 1 atm with 100 cc/min flowing nitrogen for 2 hours. The nitrogen was turned off and benzene was fed to the reactor at 60 cc/hr until reactor pressure reached the desired 2068 kPag (300 psig). Benzene flow was then reduced to 7.63 cc/hr (6.67 WHSV). Butene feed (99.28% 2-butene, 0.39% n-butane, 0.15% isobutene, and 0.18% others) was introduced from a syringe pump at 2.57 cc/hr (1.6 WHSV). Feed benzene/butene molar ratio was maintained at 3:1 for the entire run. The reactor temperature was adjusted to 160°C. Liquid products were collected at reactor conditions of 160°C and 2068 kPag (300 psig) in a cold-trap and analyzed off line. 2-Butene conversion was determined by measuring unreacted 2-butene relative to feed 2-butene. The catalyst was on stream for 4 days at 1.6 WHSV of butene with 97% 2-butene conversion, 2 days at 4.8 WHSV with 95% conversion, then 1 day at 7.2 WHSV with 86% conversion, and followed by 4 days again at 1.6 WHSV with 97% conversion. No deactivation was detected during the 11-day test cycle. Representative data are shown in Table 4. Relative activity of MCM-22 based on first-order butene conversion was 1.0.

Table 4

Days on Stream	3.8	5.9	7.1	10.8
Butene WHSV, h ⁻¹	1.6	4.8	7.2	1.6
2-Butene Conv, %	97.7	95.3	86.0	97.2
Product Selectivity, wt %				
Iso-Butane	0.010	0.001	0.004	0.008
Iso-Butene & 1-Butene	0.000	0.020	0.355	0.000
C ₅ -C ₇	0.227	0.105	0.132	0.120
C ₈ and C ₁₂ (butene oligomers)	0.812	1.753	2.556	1.910
Cumene	0.077	0.050	0.031	0.059
t-Butylbenzene	0.158	0.060	0.026	0.103
iso-Butylbenzene*	0.000	0.000	0.000	0.000
sec-Butylbenzene	89.185	90.983	90.490	91.553
n-Butylbenzene	0.024	0.031	0.030	0.025
Di-butylbenzene	8.012	6.589	5.982	5.791
Tri-butylbenzene	1.239	0.420	0.392	0.417
Heavies	0.256	0.008	0.003	0.013
Sum	100.0	100.0	100.0	100.0
Butylbenzene Composition, %				
t-Butylbenzene	0.177	0.065	0.029	0.112
iso-Butylbenzene*	0.000	0.000	0.000	0.000
sec-Butylbenzene	99.796	99.900	99.938	99.860
n-Butylbenzene	0.027	0.034	0.033	0.028
Sum	100.0	100.0	100.0	100.0

* iso-Butylbenzene less than 0.5% in total butylbenzene not detectable with GC used.

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[0047] The results in Table 4 show that, with a 2-butene feed containing only 0.15% isobutene, MCM-22 is effective in alkylating benzene at 95%+ 2-butene conversion with a selectivity to sec-butylbenzene in excess of 90%.

10 **Example 3: Sec-Butylbenzene Production Using MCM-49 Catalysts and 2-Butene Feed**

[0048] The process of Example 2 was repeated but with the MCM-22 catalyst replaced by 0.6 gm of MCM-49. The 1.3 mm (1/20 inch) quadrulobe extrudate with 60 % MCM-49/40% Versal 200 alumina binder was cut to 1.3 mm (1/20 inch) length. The catalyst was on stream for 4 days at 2.7 WHSV of butene with 97-98% butene conversion, 1 day at 8
15 WHSV with 97 % conversion, 0.5 days at 12 WHSV with 93% conversion, 1.6 days at 2.7 WHSV with 98% conversion, 0.3 days at 19.2 WHSV with 86% conversion, and followed by 0.7 days at 2.7 WHSV again with 98 % conversion. Relative activity of MCM-49 based on first-order butene conversion was 2.4. Representative data are shown in Table 5.

Table 5

Days on Stream	1.0	3.9	4.7	6.9	7.1	7.9
Butene WHSV, h ⁻¹	2.7	2.7	8.0	2.7	19.2	2.7
2-Butene Conv, %	97.6	97.3	96.7	97.7	86.3	97.6
Product Selectivity, wt %						
Iso-Butane	0.006	0.007	0.004	0.005	0.003	0.003
Iso-Butene & 1-Butene	0.000	0.000	0.000	0.000	0.358	0.000
C ₅ -C ₇	0.164	0.109	0.109	0.107	0.089	0.111
C ₈ and C ₁₂ (butene oligomers)	0.586	1.144	1.428	1.418	1.852	1.308
Cumene	0.054	0.057	0.045	0.060	0.042	0.043
t-Butylbenzene	0.125	0.128	0.069	0.105	0.042	0.091
iso-Butylbenzene*	0.000	0.000	0.000	0.000	0.000	0.000
sec-Butylbenzene	92.659	92.319	92.400	92.693	91.759	93.513
n-Butylbenzene	0.012	0.023	0.025	0.028	0.013	0.013
Di-butylbenzene	5.818	5.752	5.664	5.266	5.649	4.672
Tri-butylbenzene	0.513	0.425	0.250	0.304	0.189	0.241
Heavies	0.062	0.036	0.006	0.016	0.006	0.007
Sum	100.0	100.0	100.0	100.0	100.0	100.0
Butylbenzene Comp. %						
t-Butylbenzene	0.135	0.139	0.075	0.113	0.046	0.097
iso-Butylbenzene*	0.000	0.000	0.000	0.000	0.000	0.000
sec-Butylbenzene	99.852	99.836	99.898	99.857	99.940	99.889
n-Butylbenzene	0.013	0.025	0.027	0.030	0.014	0.014
Sum	100.0	100.0	100.0	100.0	100.0	100.0

* iso-Butylbenzene less than 0.5% in total butylbenzene not detectable with GC used.

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[0049] The results in Table 5 show that, with a 2-butene feed containing only 0.15% isobutene, MCM-49 is effective in alkylating benzene at 95%+ 2-butene conversion with a selectivity to sec-butylbenzene in excess of 92%.

10 **Example 4: Sec-Butylbenzene Production with MCM-22 Catalyst and Raffinate-2 Type Feed**

[0050] A 1.0 gram sample of the MCM-22 catalyst (65 wt% MCM-22/35% alumina binder) from Example 1 was used for the alkylation of benzene with Raffinate-2 type feed. The Raffinate-2 type feed was a synthetic blend with the following weight composition:

15 53.43% cis-butene, 41.29% trans-butene, 4.54% isobutene, 0.48% butadiene, 0.09% 1-butene, 0.09% n-butane, and 0.1% others. The catalyst was in the form of a 1.6 mm (1/16inch) diameter cylindrical extrudate and was diluted with sand to 3 cc and loaded into an isothermal, down-flow, fixed-bed, tubular reactor having an outside diameter of 4.76 mm (3/16inch). The catalyst was dried at 150°C and 1 atm with 100 cc/min flowing nitrogen for

20 2 hours. The nitrogen was turned off and benzene was fed to the reactor at 60 cc/hr until

reactor pressure reached the desired 2068 kPag (300 psig). Benzene flow was then reduced to 7.63 cc/hr (6.67 WHSV) and Raffinate-2 type feed was introduced from a syringe pump at 2.57 cc/hr (1.6 WHSV). The reactor temperature was adjusted to 160°C. Feed benzene/butene molar ratio was maintained at 3:1 for the entire run. Liquid product was collected in a cold-trap and analyzed off line. Butene conversion was determined by measuring unreacted butene relative to feed butene. The catalyst was on stream for 6 days at 1.6 WHSV of butene with 98% 2-butene conversion, 1 day at 4.8 WHSV with 80% conversion, 1 day at 7.2 WHSV with 62% conversion, and followed by 4 days again at 1.6 WHSV with 97% conversion. Representative data are shown in Table 6. Relative activity of MCM-22 based on first-order butene conversion was 0.5.

Table 6

Sample #	1	3	6	8	11	13	15
Days on Stream	0.79	2.79	5.79	7.33	8.19	9.8	11.79
Butene WHSV, h ⁻¹	1.6	1.6	1.6	4.8	7.2	1.6	1.6
2-Butene Conv, %	98.6	98.0	98.4	79.8	62.1	96.9	97.0
Isobutene Conv, %	98.2	96.3	96.8	64.4	35.8	93.7	94.0
Butadiene Conv, %	100.0	100.0	100.0	100.0	96.4	100.0	100.0
Product Selectivity, wt%							
i-C ₄	0.047	0.039	0.034	0.023	0.025	0.027	0.025
C ₅ -C ₇	0.388	0.525	0.467	0.541	0.640	0.556	0.555
C ₈ and C ₁₂ (butene oligomers)	8.739	7.886	7.746	10.343	12.852	7.916	8.230
Cumene	0.175	0.183	0.189	0.183	0.194	0.196	0.172
t-Butylbenzene	2.319	1.577	1.521	0.697	0.561	1.267	1.224
iso-Butylbenzene*	0.000	0.000	0.000	0.000	0.000	0.000	0.000
sec-Butylbenzene	81.330	83.058	83.282	82.789	81.265	83.453	83.406
n-Butylbenzene	0.034	0.059	0.055	0.063	0.058	0.060	0.062
Di-butylbenzene	5.227	5.559	5.580	4.642	3.972	5.465	5.312
Tri-butylbenzene	1.456	0.887	0.926	0.495	0.378	0.837	0.840
Heavies	0.284	0.225	0.200	0.225	0.055	0.224	0.174
Sum	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Butylbenzene Composition, %							
t-Butylbenzene	2.772	1.863	1.792	0.835	0.685	1.494	1.445
iso-Butylbenzene*	0.000	0.000	0.000	0.000	0.000	0.000	0.000
sec-Butylbenzene	97.187	97.817	98.143	99.091	99.244	98.435	98.482
n-Butylbenzene	0.041	0.070	0.064	0.075	0.071	0.071	0.073
Sum	100.0	100.0	100.0	100.0	100.0	100.0	100.0

* iso-Butylbenzene less than 0.5% in total butylbenzene not detectable with GC used.

15

[0051] Table 6 shows that the MCM-22 catalyst was effective for sec-butylbenzene production using a Raffinate-2 type feed. The 0.5% butadiene in butene feed had no significant effect on MCM-22 stability during the 12-day test cycle. However, the 4.5%

isobutene in the butene feed increased by-product formation. After initial lineout, selectivity measured at 97-98% 2-butene conversion was 8% for butene oligomers, 1.2-1.5% for t-butylbenzene, and 83% for sec-butylbenzene. This was a significant change when compared to results in Table 4 using the same catalyst and 2-butene feed. Selectivity measured with 2-butene feed at 97-98% 2-butene conversion was 1-2 % for butene oligomers, 0.1-0.2% for t-butylbenzene, and 89-91% for sec-butylbenzene. The use of Raffinate-2 type feed resulted a 50% activity drop for MCM-22.

Example 5: Sec-Butylbenzene Production with MCM-49 Catalyst and Raffinate-2 Type Feed

[0052] The process of Example 4 was repeated but with the MCM-22 catalyst replaced by 0.5 gm of MCM-49. This is the same catalyst used in Example 2. The 1.3 mm (1/20 inch) quadrulobe extrudate with 60% MCM-49/40% Versal 200 alumina binder was cut to 1.3 mm (1/20 inch) length. The MCM-49 was on stream for 3 days at 3.2 WHSV of butene with 96% conversion, 1 day at 9.6 WHSV with 80-83% conversion, and 3 days at 3.2 WHSV with 95% conversion. Representative data are shown in Table 7. Relative activity of MCM-49 based on first-order butene conversion was 1.1.

Table 7

Sample #	2	5	8
Days on Stream	2.3	3.2	5.3
Butene WHSV, h ⁻¹	3.2	9.6	3.2
2-Butene Conv, %	96.1	83.0	95.5
Isobutene Conv, %	97.7	67.2	92.8
Butadiene Conv, %	100.0	100.0	100.0
<u>Product Selectivity, wt%</u>			
i-C ₄	0.041	0.032	0.028
C ₅ -C ₇	0.527	0.503	0.583
C ₈ and C ₁₂ (butene oligomers)	7.688	9.732	8.185
Cumene	0.128	0.144	0.127
t-Butylbenzene	1.849	0.849	1.240
iso-Butylbenzene*	0.000	0.008	0.012
sec-Butylbenzene	82.977	84.284	84.720
n-Butylbenzene	0.062	0.059	0.068
Di-butylbenzene	5.431	3.878	4.273
Tri-butylbenzene	1.079	0.429	0.629
Heavies	0.218	0.082	0.134
Sum	100.0	100.0	100.0
<u>Butylbenzene Composition, %</u>			
t-Butylbenzene	2.179	0.996	1.441
iso-Butylbenzene*	0.000	0.010	0.013
sec-Butylbenzene	97.749	98.925	98.467
n-Butylbenzene	0.073	0.069	0.078
Sum	100.0	100.0	100.0

* iso-Butylbenzene less than 0.5% in total butylbenzene not detectable with GC used.

5 [0053] Table 7 shows that MCM-49 catalyst was also effective for sec-butylbenzene production using a Raffinate-2 type feed. The 0.5% butadiene in butene feed had no significant effect on MCM-49 stability during the 7-day test cycle. Again, however, the 4.5% isobutene in the butene feed increased by-product formation. Selectivity measured at 96% 2-butene conversion was 8% for butene oligomers, 1.2-1.8% for t-butylbenzene, and 83-85% for sec-butylbenzene. This is a significant change when compared to results in Table 5 using the same MCM-49 catalyst and 2-butene feed. Selectivity measured with 2-butene feed at 10 97% 2-butene conversion was 1.5 % or less for butene oligomers, 0.1% for t-butylbenzene, and 92% for sec-butylbenzene. The use of Raffinate-2 type feed resulted a 50% activity drop for MCM-49. 15

[0054] The above examples show that reducing the level of isobutene to below 0.2% in the mixed butene feed to alkylation gives reduced level of t-butylbenzene and reduced selectivity (less than 4%, typically less than 2.5%) to C8-C12 oligomers in the alkylation product.

[0055] While the present invention has been described and illustrated by reference to particular embodiments, those of ordinary skill in the art will appreciate that the invention lends itself to variations not necessarily illustrated herein. For this reason, then, reference should be made solely to the appended claims for purposes of determining the true scope of
5 the present invention.

PCT CLAIMS

1. A process for oligomerizing isobutene, the process comprising contacting a feedstock comprising isobutene with a catalyst comprising a MCM-22 family molecular sieve
5 under conditions effective to oligomerize said isobutene, said conditions including a temperature from 45°C to less than 140°C.
2. The process of claim 1 wherein said conditions include a temperature from 50°C to 120°C.
- 10 3. The process of claim 1 or 2 wherein said conditions include a pressure of from 345 to 13790 kPag (50 to 2000 psig).
4. The process of claim 3 wherein the pressure is from 1379 to 5516 kPag (200 to
15 800 psig).
5. The process of any preceding claim, wherein the molecular sieve has an X-ray diffraction pattern including d-spacing maxima at 12.4 ± 0.25 , 6.9 ± 0.15 , 3.57 ± 0.07 and 3.42 ± 0.07 Angstrom.
- 20 6. The process of any preceding claim, wherein the molecular sieve is selected from MCM-22, PSH-3, SSZ-25, ERB-1, ITQ-1, ITQ-2, MCM-36, MCM-49, MCM-56, UZM-8, and combinations of any two or more thereof.
- 25 7. The process of claim 6 wherein the molecular sieve is selected from MCM-22, MCM-49, MCM-56 and combinations of any two or more thereof.
8. The process of any preceding claim wherein the feedstock also comprises at least one additional C₄ alkene.
- 30 9. The process of claim 8 wherein the or one of the additional alkenes comprises n-butene.

10. A process for selectively oligomerizing isobutene in a hydrocarbon feedstock comprising isobutene and at least one additional C₄ alkene, the process comprising contacting the feedstock in accordance with the process of claim 8 or 9 to produce a first effluent comprising isobutene oligomers and said at least one additional C₄ alkene.

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11. The process of claim 10, wherein the at least one additional C₄ alkene comprises butene-1 and/or butene-2.

12. The process of claim 11 and further comprising separating the isobutene
10 oligomers from the first effluent to produce a second effluent rich in butene-1 and/or butene-2 and using the second effluent as a feedstock for oligomerization to produce higher olefins with low branching.

13. The process of claim 11 and further comprising using the first effluent as a
15 feedstock for the alkylation of benzene in the presence of an alkylation catalyst to produce sec-butylbenzene.

14. The process of claim 11 and further comprising separating the isobutene
20 oligomers from the first effluent to produce a second effluent rich in butene-1 and/or butene-2 and using the second effluent as a feedstock for the alkylation of benzene in the presence of an alkylation catalyst to produce sec-butylbenzene.

15. A process for producing sec-butylbenzene, the process comprising:

(a) contacting a C₄ hydrocarbon feedstock comprising isobutene and at least one
25 n-butene with a catalyst comprising a MCM-22 family molecular sieve under conditions effective to selectively oligomerize the isobutene, said conditions including a temperature from 45°C to less than 140°C and said contacting producing a first effluent comprising isobutene oligomers and said at least one n-butene;

(b) separating the isobutene oligomers from the first effluent to produce a second
30 effluent rich in said at least one n-butene;

(c) contacting the second effluent with benzene under alkylation conditions and in the presence of an alkylation catalyst to produce sec-butylbenzene.

16. The process of claim 15 wherein the C₄ hydrocarbon feedstock comprises up to 5 wt% isobutene and the first effluent contains less than 0.2 wt% isobutene.
17. The process of claim 15 or 16 wherein the C₄ hydrocarbon feedstock comprises at least 90 wt% of n-butenes and the contacting (a) oligomerizes no more than 12 wt% of the n-butenes.
18. The process of claim 15, 16 or 17 wherein the conditions in contacting (a) include a temperature from 50°C to 120°C.
19. The process of any of claims 15 to 18 wherein the conditions in contacting (a) include a pressure of from 345 to 13790 kPag (50 to 2000 psig).
20. The process of any of claims 15 to 19 and further comprising:
- (d) contacting the first effluent with water and/or an alcohol prior to said separating (b), said contacting (d) converting at least part of any isobutene remaining in said effluent to an ether.
21. The process of any of claims 15 to 20 wherein the alkylation catalyst comprises a MCM-22 family molecular sieve.
22. The process of any of claims 15 to 21 and further comprising:
- (e) oxidizing the sec-butylbenzene from (c) to produce a hydroperoxide; and
- (f) cleaving the hydroperoxide from (e) to produce phenol and methyl ethyl ketone.