

1 **METHOD OF ISOMERIZING ALPHA-OLEFINS TO LINEAR INTERNAL**
2 **OLEFINS WITH MINIMAL SKELETAL ISOMERIZATION USING**
3 **NICKEL SUPPORTED ON SILICA/ALUMINA CATALYSTS**

4 **FIELD OF THE INVENTION**

5 The present invention relates to a method of isomerizing alpha-olefins to
6 linear internal olefins with minimal skeletal isomerization.

7 **BACKGROUND OF THE INVENTION**

8 Olefins, either alpha-olefins or internal olefins, and either linear or branched,
9 have been used in drilling fluids used in the drilling of subterranean oil and
10 gas wells as well as other drilling fluid applications and drilling procedures.

11 Workers in the olefins field are searching for better, more efficient, less costly
12 ways to isomerize alpha-olefins to linear internal olefins without increasing
13 branched olefin content.

14 Several methods are known which achieve isomerization of olefins but are not
15 successful in minimizing branched olefin content and/or have other
16 disadvantages. For example, it is known that such synthetic hydrocarbons
17 can be prepared by oligomerizing one or more olefinic monomers, such as
18 those monomers having a chain length of from C₂ to C₁₄.

19 A known method for Isomerizing olefins utilizes platinum supported on a
20 SAPO-11 molecular sieve catalyst. In Gee et al. (U.S. Patent No. 5,589,442),
21 incorporated herein by reference, the platinum/SAPO-11 catalyst is used to
22 partially isomerize a feed containing C₁₄ to C₁₈ olefins, preferably linear
23 olefins, and more preferably normal alpha-olefins. The product is a mixture of
24 linear and branched olefins, with predominately internal olefins. This catalyst
25 is not effective to achieve a mixture which is essentially completely linear

- 1 internal olefins. Rather, a significant portion of the product is branched and/or
2 alpha-olefins.
- 3 Other methods are known which have similar disadvantages. For example,
4 Becker et al. (German Patent No. 4139552) teach isomerization of N-alkenes
5 to iso-alkenes using microporous aluminophosphate catalyst with inert gas
6 hydrogen and alkene-containing hydrocarbon mixture.
- 7 Khare et al. (U.S. Patent No. 5,304,696) teach double bond isomerization of
8 olefinic compounds by contacting an olefinic compound and a sulfated
9 zirconia catalyst.
- 10 Heckelsberg (U.S. Patent No. 3823572) teaches converting an olefin
11 hydrocarbon, such as propylene and/or butene, to at least one other olefin
12 hydrocarbon, such as isoamylenes, in a catalytic conversion process utilizing
13 simultaneous or sequential contacting of an olefin reaction catalyst and a
14 skeletal isomerization catalyst.
- 15 Suzukamo et al. (Japanese Patent No. 01019027) teach isomerizing olefins
16 into stable internal olefins in the presence of a solid base catalyst prepared by
17 heating at 200-450 degrees in an inert gas an alkali metal hydride and Al_2O_3
18 pretreated with an alkali metal carbonate or aluminate.
- 19 Slaugh (German Patent No. 2336138) teaches double bond isomerization of
20 normal alkenes at 20-100 degrees over a catalyst composed of a K salt on an
21 activated alumina carrier (pretreated 2-16 hours at 350-700 degrees in a
22 nonoxidizing atmosphere).
- 23 The present Applicants have found that nickel supported on a silica/alumina
24 catalyst can be used for the almost complete isomerization of alpha-olefins to
25 linear internal olefins with minimal formation of branched olefins. Such a
26 finding is a major development in the olefins field, because the nickel

1 supported on a silica/alumina catalyst is an economical alternative to
2 previously used catalysts and is actually more effective than prior art catalysts
3 used with this reaction.

4 SUMMARY OF THE INVENTION

5 In one embodiment, the present invention relates to a method of using nickel
6 supported on a silica/alumina catalyst to produce a mixture of linear internal
7 olefins from an alpha olefin feed comprising heating the feed in the presence
8 of said catalyst.

9 In a preferred embodiment of the present invention, the temperature of the
10 heating step in the above method is from 100 to 250°C.

11 In another preferred embodiment of the present invention, the heating step in
12 the above method is either a batch or continuous flow reaction.

13 In yet another preferred embodiment of the present invention, the mixture in
14 the above method is at least 80 weight % linear internal olefins.

15 In still another embodiment of the present invention, the present invention
16 relates to a method of isomerizing C₄ to C₄₀ alpha olefins to a mixture
17 comprising at least 80 weight % linear internal olefins comprising heating C₄
18 to C₄₀ alpha olefins in the presence of nickel supported on a silica/alumina
19 catalyst.

20 In a preferred embodiment of the present invention, the mixture in the above
21 method comprises at least 90 weight % linear internal olefins.

22 In a more preferred embodiment of the present invention, the mixture in the
23 above method comprises less than 5 weight % catalyst-caused skeletal
24 isomers.

1 In a yet more preferred embodiment of the present invention, the mixture in
2 the above method comprises less than 5 weight % residual alpha olefin.

3 In yet another preferred embodiment of the present invention, the heating
4 step in the above method is conducted at a temperature between 100 and
5 250°C.

6 **DETAILED DESCRIPTION OF THE INVENTION**

7 The present invention provides a method of producing linear, internal olefins
8 from alpha-olefins using nickel/aluminum catalysts.

9 **EXAMPLES**

10 The invention will be further illustrated by the following examples, which set
11 forth particularly advantageous method embodiments. While the Examples
12 are provided to illustrate the present invention, they are not intended to limit it.

13 **Example 1**

14 Linear C₁₆ alpha olefin is contacted with 100 grams of a nickel catalyst on a
15 silica/alumina catalyst in a continuous flow reactor to produce linear internal
16 olefins without significantly increasing the branch olefin content. Weight
17 Hourly Space Velocity (WHSV) is from 0.9 to 1.5. The temperature is from
18 100 to 250°C. Table 1 is a summary of the data obtained in a continuous flow
19 reactor.

Table 1

WHSV	Temp (°C)	Run duration (hours)	GC	IR
			% Skeletal isomerization *	% Alpha
1.5	200	215	0.294	4.96
1.5	200	241	1.59	3.34
1.5	200	244	1.27	3.29
1.5	200	264	1.68	2.77
1.5	200	292.5	1.88	2.98
1.5	200	316	1.69	2.83
1.5	200	343	2.67	1.99
1.5	200	366	4.5	2
1.5	200	419	1.41	3.33
1.5	200	534.5	2.8	2.01
1.5	200	581.5	2.74	2.04
1.3	185	614.5	N/A	11
0.9	185	678.5	0.21	3.73
0.9	185	705.5	0	3.97
0.9	185	749.5	0.06	3.65

*Weight percentage of skeletal isomerization introduced during isomerization.

Example 2

In comparative batch experiments, a catalyst was combined with 100 ml of C₁₆ alpha-olefin in a 250 ml round bottom flask. The reaction mixture was heated to the working temperature and stirred for the appropriate reaction time. The results are shown in Table 2 below. In Experiments 1-3, Chevron LISO, a nickel on alumina catalyst, is used which is described further in Example 4. In Experiment 4, HTC-500, a solid nickel on alumina catalyst from Crosfield, is used. In Experiment 5, Ni-3288, a solid nickel on

- 1 silica/alumina catalyst from Engelhard, is used. In Experiment 6, SAPO-11, a
2 molecular sieve, is used.

3

Table 2

Exp	Catalyst	Amt. (grams)	Time (hours)	Temp (°C)	% Alpha	% Skeletal isomeriz ation*
0	Standard 1-C ₁₈	0	0	N/A	93	0
1	Chevron LISO	6	2	220	1.1	2.65
2	Chevron LISO	6	2	130	93	0
3	Chevron LISO	6	2	200	12.8	0.4
4	HTC-500	3	4	200	93	0
5	NI-3288	3	4	200	92	0
6	SAPO-11	3	4	170	1	17.3

- 4 *Weight percentage of skeletal isomerization introduced during isomerization.

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Example 3

- 6 Linear C₁₈ alpha olefin is contacted with a nickel on silica/alumina catalyst in a
7 continuous flow reactor to produce linear internal olefins without significantly
8 increasing the branch olefin content. Weight Hourly Space Velocity (WHSV)
9 is from 0.72 to 1.52. The temperature is from 100 to 250°C. Table 3 is a
10 summary of the data obtained in a continuous flow reactor.

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Table 3**Isomerized C₁₈=Catalyst: 100 g Chevron LISO catalyst**

Run time (days)	Temp.	WHSV	%Int.	%Alpha	%Vinyl	C#C ₃₆
1	195°C	0.78	97.56	0.52	1.92	3.72
2	195°C	0.72	98.01	0.55	1.44	3.76
3	195°C	1.32	97.69	0.98	1.33	2.41
4	195°C	0.90	98.08	0.72	1.20	2.66
5	190°C	0.78	97.49	1.01	1.49	1.96
8	190°C	0.72	97.57	0.86	1.57	2.06
9	180°C	1.60	89.91	9.24	0.85	1.03
10	183°C	1.20	97.22	1.54	1.24	1.56
11	180°C		97.01	1.25	1.74	1.25
14	175°C		97.19	1.39	1.42	1.42
15	170°C	1.28	97.03	1.90	1.07	0.98
16	170°C	1.16	96.79	2.12	1.10	
18	170°C		94.71	4.22	1.06	0.85
19	170°C	1.47	89.01	10.22	0.77	0.55
21	170°C	1.40	88.70	10.48	0.84	0.51
22	175°C	1.20	86.30	13.10	0.59	
25	180°C		96.18	2.46	1.36	0.97
26	180°C	1.43	91.87	7.22	0.90	0.82
27	185°C		95.89	3.09	1.02	
28	185°C		96.06	2.79	1.16	
29	185°C		95.65	3.23	1.12	

2

1 Example 4

2 Preparation of the Chevron LISO nickel on silica/alumina catalyst

3 The catalyst is a Nickel promoted pentasil zeolite having an alumina binder.
4 The pentasil zeolite is prepared according to the teachings of U.S. patent
5 No. 3,702,886, "Crystalline Zeolite ZSM-5 and Method of Preparing the
6 Same", R. Argauer and G. Landolt, assignors to Mobil Oil Corporation. The
7 preferred composition is a zeolite having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 80 to 90.
8 The zeolite is calcined to remove the organic template, and then
9 ion-exchanged to the H-form (acid) by use of strong mineral acid such as
10 Hydrogen Chloride (HCl) to reduce the Sodium (Na) content to less than
11 100 ppm by weight. The zeolite is then compounded with a low sodium
12 alumina powder and formed into an extrudate, sphere, pellet or tablet. A
13 mixture of 70-80% zeolite dry weight basis (preferably 75%) and 20-30% dry
14 weight basis alumina powder (preferably 25%) is intensively mixed in a
15 blender, followed by addition of water, optionally containing 2-5% of nitric acid
16 for peptization of the alumina. This mixture is then extruded, pelletized,
17 spheroidized, or tabletted by methods known to those skilled in the art. The
18 preferred form is an extrudate, which may be and by use of an extruder of the
19 type manufactured by Bonnet Company. The extrudates are dried and
20 calcined at 450-550°C in a box, rotary, or belt calciner. The calcined
21 extrudates are then impregnated with a nickel salt solution to yield a nickel
22 monoxide content of 1-10% by weight of the final catalyst, and calcined at a
23 minimum of 450°C.

24 The above procedure results in a catalyst having the following properties:

Chemical Properties of LISO Catalyst

Chemical Comp. of LISO Catalyst	Weight % Basis at 537.8°C
Ni	6.0 ± 1.0
SiO ₂	66.0 ± 1.0
Al ₂ O ₃	26.4 ± 1.0
Na, ppm	≤ 150
Fe, ppm	≤ 500
Mg, ppm	≤ 500
Ca, ppm	≤ 500
C, ppm	≤ 300

Physical Properties of LISO Catalyst

Form	Extrudate
Size	1/16", 1/10" CDS, 1/8"
Compacted Bulk Density, lbs/ft ³	42 ± 3
Crush Strength, lbs./mm	≥ 2.0
BET Surface Area, m ² /g	≥ 275
Pore Volume (Hg), cm ³ /g	0.30-0.45
Attrition Resistance (ASTM)	≤ 2.0

While the present invention has been described with reference to specific embodiments, this application is intended to cover those various changes and those may make those substitutions skilled in the art without departing from the spirit and scope of the appended claims.

1 WHAT IS CLAIMED IS:

- 2 1. A method of using nickel supported on a silica/alumina catalyst to
3 produce a mixture of linear internal olefins from an alpha olefin feed
4 comprising heating the feed in the presence of said catalyst.
- 5 2. The method of claim 1 wherein the temperature of the heating steps is
6 from 100 to 250°C.
- 7 3. The method of claim 1 wherein the heating step is either a batch or
8 continuous flow reaction.
- 9 4. The method of claim 1 wherein the product mixture is at least
10 80 weight % linear internal olefins.
- 11 5. A method of isomerizing C₄ to C₄₀ alpha olefins to a mixture comprising
12 at least 80 weight % linear internal olefins comprising heating C₄ to C₄₀
13 alpha olefins in the presence of nickel supported on a silica/alumina
14 catalyst.
- 15 6. A method according to claim 5 wherein the mixture comprises at least
16 90 weight % linear internal olefins.
- 17 7. A method according to claim 5 wherein the mixture comprises less than
18 5 weight % catalyst-caused skeletal isomers.
- 19 8. A method according to claim 7 wherein the mixture comprises less than
20 5 weight % residual alpha olefin.
- 21 9. The method according to claim 5 wherein the heating step is conducted
22 at a temperature between 100 and 250°C.



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