

1 **HIGHLY HOMOGENEOUS AMORPHOUS**
2 **SILICA-ALUMINA CATALYST COMPOSITION**

3
4 FIELD OF THE INVENTION

5
6 This invention relates to improved silica-alumina catalyst compositions and to
7 a process for converting hydrocarbonaceous feed using the catalysts. More
8 specifically, this invention relates to a highly homogeneous, amorphous
9 silica-alumina cogel material, the attributes of which make it especially useful
10 for the hydroprocessing of hydrocarbonaceous feeds either alone or in
11 combination with other catalysts.

12
13 BACKGROUND OF THE INVENTION

14
15 Silica-alumina compounds are well known as catalysts used in hydrocarbon
16 conversion processes. Silica/alumina catalysts such as in the present
17 invention can be used "as is", particularly in reactions that require acidic
18 catalysts, or can optionally be combined with zeolites, clays or other binders,
19 and inorganic oxides for the cracking of liquid hydrocarbons in cracking
20 reactors such as fluid catalytic crackers and hydrocrackers. Silica-alumina
21 composites have been used commercially for a variety of hydrocarbon
22 processing applications, such as cracking, desulphurization, demetalation,
23 and denitrification.

24
25 Amorphous silica-alumina has been prepared previously by a modified cogel
26 process wherein no hydrogenation metals were added during the gellation
27 step. Spray dried, amorphous silica-alumina catalysts were made by the
28 method as described in U.S. Patent No. 4,988,659, Pecoraro to produce
29 catalysts used in hydrocarbon conversion processes.

30
31 The method of preparation of silica-alumina catalysts affects the chemical and
32 physical properties of the catalysts such as activity (such as cracking or
33 isomerization activity), and physical properties (such as pore structure and

1 volume, surface area, density and catalyst strength). Silica-alumina catalysts
2 such as in the present invention can be used "as is", particularly in reactions
3 that require acidic catalysts, or can optionally be combined with zeolites, clays
4 or other binders, and inorganic oxides for the cracking of liquid hydrocarbons
5 in cracking reactors such as fluid catalytic crackers.

6

7 Numerous silica-alumina catalyst compositions and processes for their
8 preparation are described in the patent literature. The patent literature
9 teaches a number of ways to prepare these compositions.

10 U.S. Patent No. 4,499,197, Seese et al., for example, describes the
11 preparation of inorganic oxide hydrogels, and more particularly, catalytically
12 active amorphous silica-alumina and silica-alumina rare earth cogels. The
13 active cogels are prepared by reacting aluminate and silicate solutions to
14 obtain a silica-alumina pregel, and then reacting the pregel with an acidic rare
15 earth and an aluminum salt solution with complete mixing.

16 U.S. Patent No. 4,239,651, Alfandi et al., discloses a process for preparing
17 exchanged ammoniated cogels.

18

19 U.S. Patent No. 4,289,653, Jaffe teaches preparing an extruded catalyst by
20 mixing aluminum sulfate and sulfuric acid with sodium silicate to form a silica
21 sol in an alumina salt solution at pH of 1-3, adding NH_4OH under substantially
22 constant pH of at least 4 to 6; adding more NH_4OH to form a cogelled mass to
23 pH 7.5-8.5; washing cogelled mass; mulling the mass with peptizing agent, a
24 Group VI-B metal compound and a Group VIII metal compound to form
25 extrudable dough; extruding; and drying and calcining.

26

27 U.S. Patent No. 4,988,659, Pecoraro teaches a cogelled, silica-alumina matrix
28 prepared by the method which comprises mixing a silicate solution with an
29 aqueous solution of an acid aluminum salt and an acid, to form an acidified
30 silica sol in said aluminum salt solution, and adjusting said silica sol/aluminum
31 salt solution mixture to a pH in the range of about 1 to 4; slowly adding
32 sufficient base with vigorous stirring, to said acidified silica sol/aluminum salt
33 solution mixture to form a cogel slurry of silica and alumina, and to adjust said

1 slurry to a pH in the range of about 5 to 9; aging said cogel slurry at a
2 temperature of ambient to 203°F; adjusting the pH of said cogel slurry to
3 about 5-9; recovering a cogelled mass from said slurry; washing said cogelled
4 mass; adjusting the pH of said cogelled mass to between about 4 and 7, and
5 controlling conditions to induce syneresis; and forming said combination into
6 particles.

7

8

SUMMARY OF THE INVENTION

9

10 This invention relates to a highly homogeneous amorphous silica-alumina
11 catalyst having a surface to bulk silica to alumina ratio (SB ratio) of from about
12 0.7 to about 1.3, preferably from about 0.8 to about 1.2, more preferably from
13 about 0.9 to about 1.1, and most preferably 1.0 and a crystalline alumina
14 phase present in an amount no more than about 10%, preferably no more
15 than about 5%. A catalyst of the present invention exhibits higher activity and
16 higher liquid product selectivity in comparison with other silica-alumina
17 catalysts.

18 The present invention also includes hydrocarbon conversion processing with
19 catalysts comprising the present highly homogeneous, amorphous
20 silica-alumina compositions. Examples of such hydrocarbon conversion
21 processes are well known in the art and include, but are not limited to, single
22 stage hydrocracking, two-stage hydrocracking, series-flow hydrocracking, mild
23 hydrocracking, lube hydrocracking, hydrotreating, lube hydrofinishing, olefin
24 polymerization, hydrodesulphurization, hydrodenitrification, catalytic dewaxing
25 and catalytic cracking.

26

27 A NiW catalyst prepared with one of the silica-alumina compositions of this
28 invention exhibited superior activity and distillate selectivity relative to a
29 comparable catalyst with conventional silica-alumina in a hydrocracking
30 application. The catalyst of this invention also exhibits lower gas and naphtha
31 makes, and higher total distillate yield compared to reference silica-alumina
32 catalysts.

BRIEF DESCRIPTION OF THE FIGURES

Figure 1 is a flow diagram of an example of a general procedure for preparing a silica-alumina composition of the invention.

Figure 2 is a Powder X-Ray Diffraction of various silica-alumina compositions.

DETAILED DESCRIPTION

The silica-alumina composition of the present invention is highly homogeneous. A “Surface to Bulk Si/Al Ratio” (SB Ratio) has been selected as the measure used to define the homogeneity characteristic of the silica-alumina of the present invention and to compare it with other silica-alumina compositions.

$$\text{SB Ratio} = \frac{(\text{Si/Al atomic ratio of the } \textit{surface} \text{ measured by XPS})}{(\text{Si/Al atomic ratio of the } \textit{bulk} \text{ measured by elemental analysis})}$$

To determine the SB ratio, the Si/Al atomic ratio of the silica-alumina surface is measured using x-ray photoelectron spectroscopy (XPS). XPS is also known as electron spectroscopy for chemical analysis (ESCA). Since the penetration depth of XPS is less than 50 Å, the Si/Al atomic ratio measured by XPS is for the surface chemical composition. Use of XPS for silica-alumina characterization was published by W. Daneiell et al. in Applied Catalysis A, **196**, 2000, pp 247-260. The XPS technique is, therefore, effective in measuring the chemical composition of the outer layer of catalytic particle surface. Other surface measurement techniques, such as Auger electron spectroscopy (AES) and Secondary ion mass spectroscopy (SIMS), could also be used for measurement of the surface composition.

1 Separately, the bulk Si/Al ratio of the composition is determined from
2 ICP elemental analysis. Then, by comparing the surface Si/Al ratio to the bulk
3 Si/Al ratio, the SB ratio and the homogeneity of silica-alumina are determined.
4 How the SB ratio defines the homogeneity of a particle is explained as
5 follows. An SB ratio of 1.0 means the material is completely homogeneous
6 throughout the particles. An SB ratio of less than 1.0 means the particle
7 surface is enriched with aluminum (or depleted with silicon), and aluminum is
8 predominantly located on the external surface of the particles. The SB ratio of
9 more than 1.0 means the particle surface is enriched with silicon (or depleted
10 with aluminum), and aluminum is predominantly located on the internal area
11 of the particles.

12

13 A silica-alumina composition is highly homogeneous and is a composition of
14 the present invention when its Surface to Bulk ratio (SB ratio), i.e., the ratio of
15 the Si/Al atomic ratio of the composition measured by XPS at the surface and
16 the Si/Al atomic ratio of the bulk measured by elemental analysis is from
17 about 0.7 to about 1.3, preferably from about 0.8 to about 1.2, more preferably
18 from about 0.9 to about 1.1, and most preferably 1.0.

19

20 The SB ratio of reference silica-alumina samples from two commercial
21 sources (Siral-40 from SasolCondea and MS-25 from W. R. Grace) was
22 measured and the following values were obtained:

23

24 SB ratio of Siral-40 silica-alumina = 2.1 – 2.8

25 SB ratio of MS-25 silica-alumina = 0.2 – 0.6

26

27 The above results indicate that Siral type of silica-alumina is enriched with
28 silicon on the surface of the particles (i.e., depleted with Al) as published
29 earlier by W. Daneiell et al. in Applied Catalysis A, **196**, 2000, pp 247-260. On
30 the other hand, MS-25 silica-alumina is enriched with aluminum on the
31 surface of the particles. The silica-alumina in accordance with the present
32 invention has an SB ratio of from about 0.7 to about 1.3 and is highly
33 homogeneous in that the aluminum is distributed essentially uniformly

1 throughout the particles. To maximize the activity of the silica-alumina, it is
2 most preferable to have a highly homogeneous silica-alumina having an
3 SB ratio of about 1.0.

4

5 In addition to being highly homogeneous, the silica-alumina compositions of
6 the present invention are amorphous, wherein a crystalline alumina phase,
7 such as pseudoboehmite alumina phase, is present in an amount no greater
8 than about 10%, preferably no greater than about 5%.

9

10 If the aluminum atoms are distributed uniformly throughout the particles, then
11 no separate phase of alumina would be present in the sample. Based on the
12 above hypothesis, the amount of crystalline alumina phase present in
13 silica-alumina samples was measured using an external reference of a
14 pseudoboehmite sample (relative peak area measurement similar to
15 ASTM method D3906) and the results are reported in Table 1. The percent
16 alumina phase was determined by comparing the absolute intensity of an
17 alumina peak at 14 or 38 degree 2θ .

18

19 Powder X-ray diffraction (XRD) spectrum of silica-alumina of the invention is
20 compared with that of Siral-40 silica-alumina obtained from SasolCondea and
21 shown in Figure 2. Siral-40 silica-alumina shows a significant amount of
22 crystalline alumina phase. Quantitation of the 14 and 38 degree 2θ peaks
23 indicated that Siral-40 contains approximately 48 wt% of crystalline alumina
24 phase. MS-25 silica-alumina does not exhibit crystalline alumina phase in the
25 powder X-ray diffraction. It is not highly homogeneous, however. One possible
26 reason that the MS-25 silica-alumina does not exhibit crystalline alumina
27 phase in the powder X-ray diffraction is that the low loading of aluminum in
28 the MS-25 silica-alumina (2.7 Si/Al atomic ratio) allowed the aluminum to
29 distribute uniformly on the surface. In addition to being highly amorphous,
30 silica-alumina according to the invention does not exhibit distinct crystalline
31 alumina peaks. An integration of the powder X-ray diffraction spectrum in the
32 area of 14 degree 2θ region corresponds to 0% of crystalline phase alumina.
33 This powder X-ray spectrum along with compositional information indicates

1 that the silica-alumina of the present invention is homogeneous throughout
2 the particles and amorphous.

3

4 Benefits of using a silica-alumina composition of the invention in hydrocarbon
5 conversion processing are shown by a model compound testing where the
6 catalytic activity was measured using a model feed containing 50 wt%
7 n-Hexane and 50 wt% 3-Methylpentane. The model compound testing was
8 performed at 900°F. The hydrocarbon feed vaporized in helium carrier gas
9 was flown over the 24/40 US mesh pelleted silica-alumina at
10 0.68 WHSV per g of catalytic material and conversions of the hydrocarbon
11 species were measured using Gas Chromatography. As shown in
12 Table 1, when compared to other reference silica-alumina, the silica-alumina
13 of the present invention showed significantly higher conversion activity.
14 Siral-40 silica-alumina shows 3.9 % total conversion, MS-25 silica-alumina
15 5.1% total conversion while the silica-alumina of the invention shows
16 8.2 % total conversion, which corresponds to 60-110% increase in activity.

17

18 Quantitation of the acid site using temperature programmed desorption of a
19 base such as NH_3 or isopropylamine cannot differentiate desirable silica-
20 alumina composition from the conventional silica-alumina samples. We
21 performed temperature programmed amine desorption (TPAD) of
22 isopropylamine (IPA) adsorbed in dehydrated silica-alumina samples per
23 procedures published in J. Catalysis 114, 34, 1998. The results reported in
24 Table 1 indicate that all three silica-alumina show about 0.4 mmol/g acid site
25 concentrations, and the desorbed IPA content does not correlate with the
26 above model compound testing data.

27

28 The percentages of silica and alumina in the composition overall can vary
29 widely. The composition of the silica-alumina can be changed easily to
30 provide a wide range of aluminum content from about 10 to about
31 90 wt% Al_2O_3 in the bulk. The preferred range of aluminum content is from
32 about 30 to about 70 wt% Al_2O_3 in the bulk and is most preferably about
33 46 wt% Al_2O_3 in the bulk composition which corresponds to a 1.0 Si/Al atomic

1 ratio in the gel composition so as to maximize the activity of the final
2 silica-alumina catalyst.

3

4 Silica-alumina according to the present invention may be prepared by a
5 variety of methods employing batch and continuous processes in different
6 combinations.

7

8 The two most important steps in the preparation of a silica-alumina cogel are
9 (1) preparation of the clear sol containing silica and alumina and (2) gellation
10 of the sol using a base solution. See U.S. Patent No. 4,289,653, Jaffe and
11 U.S. Patent No. 4,988,659, Pecoraro, both of which are incorporated by
12 reference herein. See also commonly assigned U.S. Patent Application titled
13 "Method for Preparing A Highly Homogenous Amorphous Silica-Alumina
14 Composition", filed concurrently herewith and incorporated by reference
15 herein.

16

17 The starting materials for the sol preparation step include aluminum salt, acid,
18 and a silica source. The aluminum salt source that can be used for the
19 synthesis includes aluminum sulfate, aluminum nitrate, aluminum chloride,
20 aluminum bromide, aluminum iodide, aluminum acetate, and aluminum metal
21 or alumina dissolved in acid. Feasible acid sources include acetic acid, formic
22 acid, sulfuric acid, hydrochloric acid, and nitric acid. The silicate sources
23 include, but are not limited to, sodium silicate, precipitated silica dissolved in a
24 base, and colloidal silica.

25

26 The sol preparation can be done either via a batch process or a continuous
27 process. It is critical to maintain the pH less than 3.0, preferably less than
28 2.5, and to ensure vigorous and complete mixing of the aluminum salt and
29 silicate solutions to minimize any unwanted gel or particle formation.

30

31 A basic precipitant such as ammonium hydroxide is then added to the
32 acidified sol solution. The addition of the precipitant raises the pH of the sol
33 above 3, resulting in cogelling the silica and alumina species. Dilute ammonia

1 solution is the preferred base for the gellation. In addition to dilute ammonia,
2 other bases such as NaOH, NaAlO₂, KOH or organic amine derivatives can
3 also be used for the gellation. It is preferable to use an inorganic base for its
4 lower cost.

5

6 The gellation step can be done either via batch process or continuous
7 process. The desirable final gellation pH is in the range of 5-9, preferably 6-8.
8 It is critical to have complete, vigorous mixing of the Si-Al solution with the
9 basic precipitant, and to maintain uniform pH throughout the mixture during
10 the precipitant addition step in order to minimize formation of isolated silica
11 domains and alumina domains.

12

13 The precipitated cogel needs to be washed to remove any unreacted
14 silicate and aluminum salt, and then it is ammonium exchanged to remove
15 sodium. The cogel should be aged for approximately 2-5 hours at room
16 temperature or at an elevated temperature of up to about 90°C and the
17 aged cogel may be spray-dried for convenience in handling and storage, or
18 may be further processed to the final catalyst from the moist state. If the
19 extrudate composition is in the dry form, such as spray-dried powders,
20 sufficient water should be added to produce a moisture content of
21 approximately 60% by weight. After mulling for approximately 1 hour,
22 optionally in the presence of peptizing acid or base, the material will attain
23 a plastic or doughy state which is suitable for extrusion in commercial
24 extrusion apparatus.

25

26 If desired, the material may be extruded, dried and calcined to produce a
27 silica-alumina catalyst or catalyst support. The preferred method of drying and
28 calcining includes an initial drying step in an air-purged oven at 65-175°C and
29 a final calcination at 480-650°F for 0.5-5 hours in a furnace or kiln. These and
30 other methods of finishing the material are set forth in U.S. Patent No.
31 4,289,653, Jaffe, incorporated by reference herein.

32

1 Other components can be combined with the cogel, for example zeolites
2 (large, intermediate, and/or small pore), other sieves such as Beta, SAPO's,
3 AIPO's etc., clays, modified clays, inorganic oxides, and oxide precursors,
4 metals, carbon, organic substances, etc. In addition, other metals may be
5 used to exchange residual Na_2O . In these compositions the cogels have been
6 found to be excellent matrices for FCC applications, as well as excellent
7 supports for hydroprocessing applications.

8
9 The present invention also includes hydrocarbon conversion processing with
10 catalysts comprising the present highly homogeneous, amorphous
11 silica-alumina compositions. Examples of such hydrocarbon conversion
12 processes in which the subject silica-alumina catalysts may be used are well
13 known in the art and include, but are not limited to, single stage
14 hydrocracking, two-stage hydrocracking, series-flow hydrocracking, mild
15 hydrocracking, lube hydrocracking, hydrotreating, lube hydrofinishing, olefin
16 polymerization, hydrodesulphurization, hydrodenitrification, catalytic dewaxing
17 and catalytic cracking.

18
19 The present invention also provides a process for converting hydrocarbons
20 comprising contacting a hydrocarbonaceous feed at hydrocarbon converting
21 conditions with a catalyst comprising highly homogeneous amorphous
22 silica-alumina catalyst having a Surface to Bulk Si/Al ratio of from about
23 0.7 to about 1.3, preferably from about 0.8 to about 1.2, more preferably from
24 about 0.9 to about 1.1, and most preferably 1.0 and a crystalline alumina
25 phase present in an amount no more than about 10%, preferably no more
26 than about 5%.

27
28 The present invention also provides a hydrocracking process comprising
29 contacting the catalyst of the invention with a hydrocarbon feedstock under
30 hydrocracking conditions.

31

1 The present invention also provides a catalytic dewaxing process comprising
2 contacting the catalyst of the invention with a hydrocarbon feedstock under
3 dewaxing conditions.

4

5 The present invention also provides a process for catalytically dewaxing a
6 hydrocarbon oil feedstock boiling above about 650°F and containing straight
7 chain and slightly branched chain hydrocarbons comprising contacting said
8 hydrocarbon oil feedstock in the presence of added hydrogen gas at a
9 hydrogen pressure of about 500-3000 psig under dewaxing conditions with
10 the catalyst of the invention.

11

12 The present invention also provides a process for lube oil hydrofinishing
13 comprising contacting the catalyst of the invention with a hydrocarbon oil
14 feedstock boiling above about 650°F under hydrogenation conditions in to
15 produce a lubricating oil base stock.

16

17 The present invention also provides a catalytic cracking process comprising
18 contacting a hydrocarbon feedstock in a reaction zone under catalytic
19 cracking conditions in the absence of added hydrogen with the catalyst of the
20 invention.

21

22 The process conditions and other catalyst components useful with the
23 silica-alumina catalysts of the present invention are well known in the art.
24 Representative examples are disclosed U.S. Patent Nos. 4,910,006,
25 4,921,594, 5,316,753, 5,393,410, 5,834,572, 5,993,644 and 6,264,826 which
26 are incorporated by reference herein in their entirety.

27

28 Feedstocks which can be suitably employed in the process according to the
29 present invention comprise gas oils, vacuum gas oils, deasphalted oils,
30 long residues, catalytically cracked cycle oils, coker gas oils and other
31 thermally cracked gas oils and syncrudes, optionally origination from tar
32 sands, shale oils, waxy hydrocarbons from Fisher-Tropsch hydrocarbon

1 synthesis process, residue upgrading processes or biomass. Combinations of
2 various feedstocks can also be employed.

3

4 The following Examples are illustrative of the present invention, but are not
5 intended to limit the invention in any way beyond what is contained in the
6 claims which follow.

1 **Example 1:** Synthesis of Silica-Alumina of the invention by batch gellation

2

3 An acidic aluminum solution (Solution I containing 7.3 wt% Al_2O_3) was
4 prepared by dissolving 1089 g of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ and 205 g of acetic acid (99.9%
5 concentrated) in 1857 g of deionized water. A dilute solution of sodium silicate
6 (Solution II containing 5 wt% SiO_2) was prepared by diluting 931 g of
7 concentrated sodium silicate solution (contains 29 wt% SiO_2 and 9% Na_2O)
8 with deionized water. The silicate solution was gradually added to the
9 aluminum solution while vigorously mixing to prepare Solution III. It is
10 desirable to maintain the pH below 3.0 to ensure formation of clear sol of
11 silica and alumina. The final pH of the Solution III was 2.2, and the mixing
12 produced a clear silica and alumina solution. The final Solution III contained:

13

14 $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 2.0

15 H^+/Na^+ molar ratio of 1.1

16

17 Diluted ammonia solution (Solution IV containing 8 wt% NH_3) was prepared
18 for gellation. The diluted ammonia solution was added gradually to Solution III
19 containing silica and alumina sol while vigorously mixing. Cogelled
20 silica-alumina started to precipitate when the pH of the slurry reached at about
21 3.2, and then gellation completed when the pH reached at about 7. We
22 continued the ammonia solution addition until the pH of the slurry reached
23 8.0. The gel slurry was aged at room temperature for 3 hours while stirring.
24 This cogelled silica-alumina was filtered to produce a filtered cake. The cake
25 was washed with a hot solution of ammonium acetate (3.8 wt%, 10 L solution,
26 125°F) for 15 minutes, and then rinsed with 10 L of deionized water. The
27 washing step was repeated four more times. The final cake was dried at
28 250°F overnight. A small amount of the dried silica-alumina cake was crushed
29 to small pieces and calcined under excess dry air at 1000°F for 1 hour for
30 activation. Physical properties of the final silica-alumina are summarized in
31 Table 1.

1 **Table 1**
 2 **Physical Properties and Conversion Activity of Silica-Alumina Compositions**

	Silica-Alumina Invention (<i>Example 1</i>)	Reference, <i>Siral-40 Silica-Alumina</i>	Reference, <i>MS-25 Silica-Alumina</i>
Surface area, m ² /g (a)	362	513	486
Total pore volume, cc/g (b)	0.51	0.83	0.80
Pore size distribution by N ₂ Adsorption (b)			
30 Å-, %	8.6	7.9	5.9
30 – 60 Å, %	55.5	30.5	45.0
60 - 100 Å, %	32.9	32.8	39.9
100 - 200 Å, %	1.4	18.6	8.3
200 - 300 Å+, %	0.4	4.2	0.4
300 Å+, %	1.2	5.9	0.5
Mean Pore Diameter, Å	69	113	75
Na, wt%	<0.05	<0.05	<0.05
Surface Si/Al atomic ratio, by XPS	0.98	1.17	1.31
Bulk Si/Al atomic ratio, by elemental anal.	1.03	0.57	2.74
Surface to Bulk Si/Al Ratio	0.95	2.05	0.48
% crystalline alumina phase, by XRD	0 %	48 %	0 %
nC ₆ + iC ₆ Model Compound Testing (b)			
Total conversion, wt%	8.2	3.9	5.1
nC ₆ conversion, wt%	1.0	0.8	0.9
iC ₆ conversion, wt%	15.4	7.1	9.4
Isopropylamine TPAD, mmol/g	0.43	0.35	0.49

3 (a): BET measurements after activation at 1000° F for 1 hr.

4 (b): determined after activation at 1000° F for 1 hr.

1 **Example 2:** Synthesis of Silica-Alumina of the Invention by Continuous

2 Gellation

3

4 An acidic aluminum solution (Solution I containing 6 wt% Al_2O_3) was prepared
5 by dissolving 3127 g of $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$ and 338 g of sulfuric acid
6 (98% concentrated) in 4968 g of deionized water. A dilute solution of sodium
7 silicate (Solution II containing 6 wt% SiO_2) was prepared by diluting 2070 g of
8 concentrated sodium silicate solution (contains 29wt% SiO_2 and 9% Na_2O)
9 with deionized water. The silicate solution was gradually added to the
10 aluminum solution while vigorously mixing to prepare Solution III. The final pH
11 of the Solution III was 2.1, and the mixing produced a clear silica and alumina
12 solution. The final Solution III contained:

13

14 $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 2.0

15 H^+/Na^+ molar ratio of 1.2

16

17 Diluted ammonia solution (containing 8 wt% NH_3) was prepared for gellation.
18 The dilute ammonia solution and the Solution III containing the silica and
19 alumina sol were pumped separately and simultaneously into the mixing
20 chamber of an in-line blender. Mixing in the in-line blender was vigorous with
21 1600-RPM blender-blade rotation. The volume of the mixing chamber is
22 smaller than the total volume of solutions pumped in 1 minute (i.e., less than
23 1 minute residence time per volume). The addition rate of the ammonia
24 solution was adjusted to maintain the pH of the gel product at 7 ± 0.5 . The gel
25 slurry was collected and then aged at room temperature for 2 hours while
26 stirring. This cogelled silica-alumina was filtered to produce a filtered cake.
27 The cake was washed with a hot solution of ammonium sulfate (5 wt%,
28 10 L solution) for 15 minutes, and then rinsed with 10 L of deionized water.
29 The washing step was repeated four more times. The final cake was dried at
30 250°F overnight. A small amount of the silica-alumina was crushed to small
31 pieces and calcined under excess dry air at 1000°F for 1 hour for activation.
32 Physical properties of the final silica-alumina are summarized in Table 2.

1 **Example 3:** Synthesis of Silica-Alumina of the Invention by continuous sol
2 preparation followed by continuous gel preparation

3
4 This silica-alumina was identical in composition to that prepared in Example 2,
5 but the preparation procedure was different. In this example, the in-line
6 blender from Example 2 was used to prepare Solution III, a clear solution
7 containing silica and alumina sol, as well as for the final continuous gellation.

8
9 The alumina/sulfuric acid solution (Solution I) and the silicate solution
10 (Solution II) were pumped separately and simultaneously into the mixing
11 chamber of an in-line blender while vigorously mixing. Mixing in the in-line
12 blender was vigorous with 1600-RPM blender-blade rotation. The pH of the
13 combined solution ranged 1.9-2.0. Then the product from the in-line blender
14 (Solution III containing the silica and alumina sol) and the dilute ammonia
15 solution were pumped separately and simultaneously into the mixing chamber
16 of a second in-line blender for gel formation. The rate of the ammonia solution
17 was adjusted to maintain the pH of the gel product at 7 ± 0.5 . The mixing in
18 the in-line blender was again vigorous with 1600-RPM blender-blade rotation.
19 The gel product was collected and then aged at room temperature for 2 hours
20 while stirring. This cogelled silica-alumina was filtered to produce a filtered
21 cake. The cake was washed with a hot solution of ammonium sulfate (5 wt%,
22 10 L solution) for 15 minutes, and then rinsed with 10 L of deionized water.
23 The washing step was repeated four more times. The final cake was dried at
24 250°F overnight. A small amount of the silica-alumina was sized to small
25 pieces and calcined under excess dry air at 1000°F for 1 hour for activation.
26 Physical properties of the final silica-alumina are summarized in Table 2.

Table 2
Physical Properties and Conversion Activity of a
Silica-Alumina of the Invention Prepared by a Continuous Process

	Silica-Alumina Invention (<i>Example 2</i>)	Silica-Alumina Invention (<i>Example 3</i>)
Surface area, m ² /g (a)	418	367
Total pore volume, cc/g (b)	0.55	0.77
<u>Pore size distribution by N₂ Adsorption (b)</u>		
30 Å-, %	11.4	8.2
30 – 60 Å, %	54.7	22.9
60 - 100 Å, %	25.2	17.2
100 - 200 Å, %	6.3	23.3
200 - 300 Å+, %	1.0	11.1
300 Å+, %	1.4	17.3
Mean Pore Diameter, Å	71	187
Na, wt%	<0.05	<0.05
Surface Si/Al atomic ratio, by XPS	1.07	1.21
Bulk Si/Al atomic ratio, by elemental anal.	1.03	0.96
Surface to Bulk Si/Al Ratio	1.04	1.26
% crystalline alumina phase, by XRD	0 %	5 %
<u>nC₆ + iC₆ Model Compound Testing</u>		
Total conversion, wt%	11.3	8.6
nC ₆ conversion, wt%	1.3	1.2
iC ₆ conversion, wt%	21.3	16

The continuous preparations of Example 2 and Example 3 produced high quality silica-alumina with uniform composition. They exhibited high surface areas of 418 and 367 m²/g. The continuous gellation prep (Example 2) produced a composition with the pore size distribution nearly identical to the sample produced via batch gellation (Example 1). The continuous sol/continuous gel preparation produced a silica-alumina of the invention with much larger pores (Example 3). The mean pore diameter is 187 Å for silica-alumina made by the continuous sol/ continuous gel preparation, and 69 and 71 Å for silica-alumina prepared by the batch gellation and continuous gellation, respectively. All silica-alumina samples showed excellent activity for

1 hydrocarbon conversion as shown with the model compound testing.
2 Example 2 showed 11.3% total hydrocarbon conversion and Example 3
3 8.6% conversion, comparable to the sample prepared via batch gelation.
4

5 **Example 4:** (Comparative) Preparation of NiW Hydrocracking Catalyst with
6 Silica-Alumina (Catalyst A – base-case)
7

8 A base-case hydrocracking catalyst containing Siral-40, the reference
9 silica-alumina from Table 1, was prepared per following procedure.
10 75 parts silica-alumina powder (Siral-40, obtained from SasolCondea) and
11 25 parts pseudoboehmite alumina powder (obtained from Vista) were mixed
12 well. To the mix, diluted HNO₃ acid and sufficient amount of deionized water
13 were added to form an extrudable paste (3 wt% HNO₃ to the total powders).
14 These weights are on 100% solids basis. The paste was extruded in
15 1/16" cylinder, and dried at 250°F overnight. The dried extrudates were
16 calcined at 1100°F for 1 hour with purging excess dry air, and cooled down to
17 room temperature.
18

19 Impregnation of Ni and W was done using a solution containing ammonium
20 metatungstate and nickel nitrate to the target metal loadings of 4 wt% NiO and
21 28 wt% WO₃ in the finished catalyst. The total volume of the solution matched
22 the 100% water pore volume of the base extrudate sample (incipient wetness
23 method). The metal solution was added to the base extrudates gradually while
24 tumbling the extrudates. When the solution addition was complete, the soaked
25 extrudates were aged for 2 hours. Then the extrudates were dried at 250°F
26 overnight. The dried extrudates were calcined at 935°F for 1 hour with purging
27 excess dry air, and cooled down to room temperature. This catalyst is named
28 Catalyst A and its physical properties are summarized in Table 4.
29

30 Catalyst B, a NiW catalyst containing silica-alumina of the invention, was
31 prepared using a procedure similar to Catalyst A. For Catalyst B, 80 parts
32 silica-alumina of the invention from Example 1 and 20 parts pseudoboehmite

1 alumina were used to prepare the base extrudates. The target metal loadings
2 were 4 wt% Ni and 20 wt% W.

3

4 Catalyst C, a silica-alumina containing silica-alumina of the invention was
5 prepared using a procedure nearly identical to Catalyst A. For Catalyst C,
6 silica-alumina of the invention from Example 3 was used to prepare the base
7 extrudates. Physical properties of Catalyst B and C are summarized in
8 Table 4.

9

10 A petroleum feedstock with the following properties (Table 3) was used to
11 evaluate the catalysts.

12

13

14

Table 3
Feedstock Properties

Properties	
API Gravity	33.7
Sulfur, ppm wt	7
Nitrogen, ppm wt	0.7
D2887 Simulated Distillation	
IBP	645°F
10 wt%	707°F
30 wt%	769°F
50 wt%	826°F
70 wt%	890°F
90 wt%	977°F
End Point	1079°F

15

16 Micro unit evaluation of catalysts was done in a once-through, down-flow
17 micro unit with 6 cc of 24/40 (US) meshed catalyst. Process conditions were
18 approximately 2000 psig reactor pressure, a feed rate of 1.5 hour⁻¹ LHSV and
19 once-through H₂ flow rate corresponding 5000 SCF of H₂/ bbl of oil. The
20 catalyst bed temperature was varied to cover 60-80 wt% of conversion of the
21 700°F⁺ feed to 700°F⁻ product. The yields of C₄⁻ gas, naphtha, and light and
22 heavy distillate components were calculated using D2887 Simdis analysis
23 results. The overall yields and reactor temperature data were interpolated to
24 70 wt% conversion and summarized in Table 4.

25

1 Catalysts of the invention (Catalysts B and C) showed much higher activity
 2 than the base case catalyst made with a commercial silica-alumina
 3 (Catalyst A). A catalyst of the invention achieved the same conversion at
 4 23-24°F lower reactor temperatures (Table 4). In addition, liquid product
 5 selectivity is also favored by catalysts of invention in that about 1 wt%
 6 advantage in the distillate yield was observed. Such high activity advantage
 7 and at the same time better distillate selectivity are quite unexpected benefits
 8 of silica-alumina of the present invention.

10 **Table 4**
 11 **Catalyst Properties and Performance**

	Catalyst A Non-Invention	Catalyst B Invention	Catalyst C Invention
<u>Composition (before metals addition)</u>			
Silica-Alumina	75% Siral-40	80% silica- alumina (Example 1)	75% silica- alumina (Example 3)
Al ₂ O ₃ Binder	25% Catapal B	20% Catapal B	25% Catapal B
<u>Properties after Metals Addition</u>			
Ni, wt%	3.2	3.9	3.3
W, wt%	21.4	18.7	21.6
Surface area, m ² /g	229	182	166
<u>Catalyst Performance in Single-Pass Micro Unit</u>			
Activity, °F, for 70% Conversion	741	717	718
<u>Yields @ 70% Conv., wt%</u>			
C ₄ Gas	3.3	2.9	2.8
Naphtha (C5 – 250°F)	13.1	12.8	12.8
Light Distillate (250°F – 550°F)	36.4	37.2	37.4
Heavy Distillate (550°F – 700°F)	21.3	21.1	21.0
Total Distillate (250°F – 700°F)	57.7	58.3	58.5

12
 13 While not wanting to be bound by any specific theory, the performance
 14 advantage of the catalyst of the invention appears to come from maximizing
 15 the number of the available acid sites in the silica-alumina composition. This
 16 was achieved by having a highly homogeneous distribution of aluminum
 17 throughout the silica-alumina particles. As a result, the silica-alumina of the
 18 present invention exhibits much higher activity than conventional
 19 silica-alumina. Typically, higher activity is connected to poorer selectivity for

1 distillate. Surprisingly, on the contrary catalysts of the present invention
2 exhibit the additional benefit of improved distillate yield, indicating enhanced
3 isomerization activity.

4

5 There are numerous variations on the present invention which are possible in
6 light of the teachings and supporting examples described herein. It is
7 therefore understood that within the scope of the following claims, the
8 invention may be practiced otherwise than as specifically described or
9 exemplified herein.

1 WHAT IS CLAIMED IS:

2

3 1. A highly homogeneous amorphous silica-alumina catalyst having a
4 Surface to Bulk Si/Al ratio of from about 0.7 to about 1.3 and wherein a
5 crystalline alumina phase is present in an amount of no greater than
6 about 10%.

7

8 2. A silica-alumina catalyst according to claim 1, wherein the Surface to
9 Bulk Si/Al ratio is from about 0.8 to about 1.2.

10

11 3. A silica-alumina catalyst according to claim 1, wherein the Surface to
12 Bulk Si/Al ratio is from about 0.9 to about 1.1.

13

14 4. A silica-alumina catalyst according to claim 1, wherein the crystalline
15 alumina phase is present in an amount of no greater than about 5%.

16

17 5. A silica-alumina catalyst according to claim 1, wherein the catalyst
18 comprises from about 10 weight percent to about 90 weight percent
19 Al₂O₃.

20

21 6. A silica-alumina catalyst according to claim 1, wherein the catalyst
22 comprises from about 30 weight percent to about 70 weight percent
23 Al₂O₃.

24

25 7. A silica-alumina catalyst according to claim 1, wherein the catalyst
26 comprises about 46 weight percent Al₂O₃.

27

28 8. A silica-alumina catalyst according to claim 1, further comprising a
29 binder.

30

31 9. A process for converting hydrocarbons comprising contacting a
32 hydrocarbonaceous feed at hydrocarbon converting conditions with a
33 catalyst comprising highly homogeneous amorphous silica-alumina

- 1 catalyst having a Surface to Bulk Si/Al ratio of from about 0.7 to about
2 1.3 and wherein an alumina phase is present in an amount of no
3 greater than about 10%.
4
- 5 10. The process of claim 9, wherein the process is a hydrocracking
6 process comprising contacting the catalyst with a hydrocarbon
7 feedstock under hydrocracking conditions.
8
- 9 11. The process of claim 9, wherein the process is a dewaxing process
10 comprising contacting the catalyst with a hydrocarbon feedstock under
11 dewaxing conditions.
12
- 13 12. The process of claim 9, wherein the process is a process for
14 catalytically dewaxing a hydrocarbon oil feedstock boiling above about
15 650 °F and containing straight chain and slightly branched chain
16 hydrocarbons comprising contacting the catalyst with a hydrocarbon oil
17 feedstock in the presence of added hydrogen gas at a hydrogen
18 pressure of about 500-3000 psig under dewaxing conditions with the
19 catalyst.
20
- 21 13. The process of claim 9, wherein the process is a catalytic cracking
22 process comprising contacting the catalyst with a hydrocarbon
23 feedstock in a reaction zone under catalytic cracking conditions in the
24 absence of added hydrogen.
25
- 26 14. The process of claim 9, wherein the process is a lube oil hydrofinishing
27 process comprising contacting the catalyst with a hydrocarbon oil
28 feedstock boiling above about 650 °F under hydrogenation conditions
29 to produce a lubricating oil base stock.
30
- 31 15. The process of claim 9, wherein the hydrocarbon feedstock is selected
32 from the group consisting of gas oils, vacuum gas oils, deasphalted
33 oils, long residues, catalytically cracked cycle oils, coker gas oils, other

- 1 thermally cracked gas oils, syncrudes shale oils, waxy hydrocarbons
- 2 from Fischer-Tropsch hydrocarbon synthesis process, residue
- 3 upgrading processes or biomass and mixtures thereof.