

1 **HOMOGENEOUS MODIFIED-ALUMINA**
2 **FISCHER-TROPSCH CATALYST SUPPORTS**

3
4 FIELD OF THE INVENTION

5
6 This invention relates to improved catalyst supports. More specifically, this
7 invention relates to a homogeneous, amorphous modified-alumina cogel
8 material, the attributes of which make it especially useful for use as a support
9 for Fischer-Tropsch catalysts.

10
11 BACKGROUND OF THE INVENTION

12
13 The preparation of hydrocarbons from synthesis gas is well known in the art
14 and is usually referred to as Fischer-Tropsch synthesis, the Fischer-Tropsch
15 process, or Fischer-Tropsch reaction(s). Catalysts for use in such synthesis
16 usually contain a catalytically active Group VIII metal supported on a carrier.
17 The support may be alumina, silica, titania, zirconia, magnesia and their
18 mixtures. The Group VIII metals, iron, cobalt, nickel, and ruthenium have been
19 often used as the catalytically active metals. Cobalt and iron have been found
20 to be most suitable for catalyzing a process in which synthesis gas is
21 converted to primarily hydrocarbons having five or more carbon atoms.
22 Additionally, the catalysts often contain one or more promoters. The catalyst
23 promoter may be a basic oxide such as ThO₂, La₂O₃, MgO, ZrO₂, and TiO₂,
24 although promoters may also comprise noble metals such as Pt, Pd, Ru, Rh,
25 Os, and Ir; coinage metals such as Cu, Ag, and Au; and other transition
26 metals such as Fe, Mn, Ni, and Re. Fischer-Tropsch catalysts and processes
27 are described in U.S. Patent Nos. 6,476,085; 6,586,481; and 4,568,663. The
28 active metal may be incorporated into the base by impregnation, drying and
29 calcination as disclosed in U.S. Patent Application 2003/0162849 A1 to van
30 Berge et al.

31
32 Alumina is one of the most desirable supports in catalysis. Due to its high
33 surface area and good mechanical properties, particularly gamma form of

1 alumina has been used widely in industry for many catalytic applications.
2 However, in an acidic or alcohol containing reaction medium such as
3 Fischer-Tropsch synthesis conditions to produce wax, or other reactions
4 proceeding in aqueous medium such as alcohol, ether, and ester syntheses,
5 an alumina support exhibits a stability problem. Alumina may dissolve or leach
6 slowly in the reactor due to attacks of acid and alcohol byproducts in the
7 reaction medium. Dissolution of alumina support in acid medium is expected
8 to be detrimental in catalyst stability. The dissolution problem may cause poor
9 maintenance of catalyst integrity and possible fines generation. Possible fines
10 generation will hurt the subsequent filtration and post processing operations.
11 High metal or metal compound content in a Fischer-Tropsch product is
12 undesirable because such contaminants could have adverse effects for the
13 Fischer-Tropsch process, such as causing reactor plugging or significantly
14 reducing catalyst life. As a result, it is important that the product of the
15 Fischer-Tropsch process be free of metal and other contaminants that could
16 adversely affect its subsequent processing.

17

18 Thus it is highly desirable to have a catalyst support with the favorable
19 characteristics of an alumina support with much improved acid resistance.

20

21 U.S. Patent No. 5,733,839 to van Berge et al. shows that silica coating on
22 gamma alumina particles improves dissolution tendency of alumina and the
23 silica-coated alumina support is useful as a Fischer-Tropsch synthesis
24 catalyst. U.S. Patent Application 2003/0162849 A1 to van Berge et al. shows
25 that silica-coated alumina prepared via *in situ* coating in a slurry of aluminum
26 hydroxylate prior to spray drying is also useful as a support for a
27 Fischer-Tropsch synthesis catalyst. Daniell et al. studied the latter material in
28 depth using FT-IR and XPS and showed that little mixing of the two oxide
29 phases take place on the surface so the surface can be depicted as
30 comprising two separate oxide phases (Applied Catalysis A: 196, 247-260,
31 2000).

SUMMARY OF THE INVENTION

This invention relates to a homogeneous, amorphous catalyst support comprising a modifying-metal-oxide and a base-metal oxide, in which the modifying-metal-oxide is homogeneously distributed throughout the base-metal oxide, the catalyst support having a Surface to Bulk modifying-metal /base-metal atomic ratio of from about 0.6 to about 1.3 and exhibiting an X-ray diffraction having broader line width and lower intensity than is exhibited by the base-metal oxide. More specifically, the present invention relates to a homogeneous, amorphous silica-modified-alumina catalyst support having a Surface to Bulk Si/Al ratio of from about 0.6 to about 1.3 and exhibiting an X-ray diffraction having broader line width and lower intensity than is exhibited by unmodified alumina. A silica-modified-alumina catalyst support of the present invention maintains the desirable properties of alumina and exhibits higher resistance to acid than unmodified alumina.

In a first aspect, there is provided a homogeneous, amorphous cogel catalyst support comprising a modifying-metal-oxide and a base-metal oxide, wherein the modifying-metal-oxide is homogeneously distributed throughout the base-metal oxide, the catalyst support having a Surface to Bulk modifying-metal /base-metal atomic ratio of from about 0.9 to about 1.1 and exhibiting an X-ray diffraction having broader line width and lower intensity than is exhibited by the base-metal oxide.

In a second aspect, there is provided a homogeneous, amorphous silica-modified-alumina cogel catalyst support having a Surface to Bulk Si/Al ratio of from about 0.9 to about 1.1 and exhibiting an X-ray diffraction having broader line width and lower intensity than is exhibited by unmodified alumina.

In a third aspect, there is provided a homogeneous, amorphous silica-modified-alumina catalyst support exhibiting an X-ray diffraction having a broader line width and lower intensity than is exhibited by unmodified alumina.

BRIEF DESCRIPTION OF THE FIGURES

Figure 1 is a Powder X-ray diffraction of alumina and silica-modified alumina.

Figure 2 is a graph showing conductivity change as a function of time.

DETAILED DESCRIPTION

The following detailed description is made with reference to a preferred embodiment of the invention, a silica-modified alumina Fischer-Tropsch catalyst support. It is not the intention that the invention be construed in this limited fashion. Other metal oxides may be used as support materials. For example, the base-metal oxides may be alumina, silica, titania and their mixtures. The base-metal oxides may be modified with modifying-metal-oxides such as silica, titania, zirconia, magnesia and their mixtures. The materials described may be used as a catalyst support for

1 catalysts other than Fischer-Tropsch catalysts. Other variations will be
2 apparent to the skilled artisan base on the description herein.

3

4 As more fully described herein, an acid resistant alumina support is prepared
5 by cogellation of a homogeneous solution containing alumina and a small
6 amount of silica. Upon calcination, the process produces gamma-type
7 amorphous alumina with silicon dioxide incorporated uniformly throughout the
8 structure. Aluminum leaching of this catalyst by acid attack is significantly
9 reduced in this homogeneous silica-modified alumina support. This type of
10 support may show advantages over the silica-coated alumina support when
11 the reaction conditions are vigorous and cause attrition of catalyst particles. A
12 silica-coated alumina support may lose its coating upon attrition in a reactor,
13 whereas a catalyst support in accordance with the present invention will
14 maintain its acid resistance uniformly throughout.

15

16 As noted previously, the base support may be composed of alumina, silica,
17 titania, magnesia and their mixtures. Alumina is the preferred base-metal
18 oxide. Where the base support is alumina, the alumina component may have
19 any phase form selected from eta, gamma, delta, theta, alpha and their
20 mixtures, it is preferred that the base support is alumina in the gamma phase.
21 The base material in the support is generally present in concentrations of from
22 about 70 wt% or greater. Desirable base support content is from about
23 70 - 99.75 wt% of base-metal oxide, preferably 80 - 99.5 wt%, and most
24 preferably 90 - 99 wt%.

25

26 Silica is the preferred modifier for alumina. Alternative modifiers can be titania,
27 zirconia, magnesia, and mixtures thereof. Desirable modifier content is from
28 about 0.25 - 30 wt% of modified oxide, preferably 0.5 - 20 wt%, and most
29 preferably 1 - 10 wt%. The modified-alumina composition of the present
30 invention is homogeneous. This means that silicon dioxide is incorporated
31 uniformly throughout the structure of the particles. Two different indicators are
32 described that demonstrate that silicon dioxide incorporation is uniform and
33 that the composition is homogeneous.

1 First, a "Surface to Bulk Si/Al Ratio" (SB Ratio) is a measure used to indicate
2 that the modified-alumina of the present invention is homogeneous.

3

4

$$\begin{array}{l} 5 \quad \text{SB Ratio} = \frac{(\text{Si/Al atomic ratio of the } \textit{surface} \text{ measured by XPS})}{(\text{Si/Al atomic ratio of the } \textit{bulk} \text{ measured by elemental analysis})} \\ 6 \end{array}$$

7

8

9 To determine the SB ratio, the Si/Al atomic ratio of the silica-modified alumina
10 surface is measured using x-ray photoelectron spectroscopy (XPS). XPS is
11 also known as electron spectroscopy for chemical analysis (ESCA). Since the
12 penetration depth of XPS is less than 50 Å, the Si/Al atomic ratio measured by
13 XPS is for the surface chemical composition. Use of XPS for silica-alumina
14 characterization was published by W. Daniell et al. in Applied Catalysis A,
15 **196**, 2000, pp 247-260. The XPS technique is, therefore, effective in
16 measuring the chemical composition of the outer layer of catalytic particle
17 surface. Other surface measurement techniques, such as Auger electron
18 spectroscopy (AES) and Secondary ion mass spectroscopy (SIMS), could
19 also be used for measurement of the surface composition.

20

21 Separately, the bulk Si/Al ratio of the composition is determined from
22 ICP elemental analysis. Then, by comparing the surface Si/Al ratio to the bulk
23 Si/Al ratio, the SB ratio and the homogeneity of the material is determined.
24 How the SB ratio defines the homogeneity of a particle is explained as
25 follows. An SB ratio of 1.0 means the material is completely homogeneous
26 throughout the particles. An SB ratio of less than 1.0 means the particle
27 surface is enriched with aluminum (or depleted with silicon), and aluminum is
28 predominantly located on the external surface of the particles. The SB ratio of
29 more than 1.0 means the particle surface is enriched with silicon (or depleted
30 with aluminum), and aluminum is predominantly located on the internal area
31 of the particles.

1 A silica-modified-alumina composition is homogeneous when its Surface to
2 Bulk ratio (SB ratio), i.e., the ratio of the Si/Al atomic ratio of the composition
3 measured by XPS at the surface and the Si/Al atomic ratio of the bulk
4 measured by elemental analysis is from about 0.6 to about 1.3. The SB ratio
5 is preferably from about 0.8 to about 1.2, more preferably from about 0.9 to
6 about 1.1, and most preferably 1.0.

7
8 A second indicator of the homogeneity of the silica-modified-alumina of the
9 present invention is the breadth of the linewidth of the X-Ray Diffraction
10 peaks. As will be seen in the Examples, the linewidth of each or the XRD
11 peaks is significantly broader for the silica-modified-alumina as compared to a
12 reference unmodified alumina. For example, the full-width-at-half-height
13 (FWHH) of the 38.5 degree 2θ peak, showed a linewidth that was increased
14 by 113% compared to the reference alumina.

15
16 In addition to being homogeneous, the silica-modified-alumina compositions
17 of the present invention are amorphous, having a lower relative crystallinity
18 than the reference unmodified alumina. The amorphous nature of the
19 compositions of the present invention is shown by comparing the X-ray
20 diffraction patterns of modified and unmodified compositions. As will be seen
21 further in the Examples, the silica-modified-alumina has an overall intensity
22 substantially lower than the reference alumina, which indicates that is more
23 amorphous than the reference. In one instance, the relative crystallinity was
24 estimated to be 58% of the reference by integrating the 38.5 degree 2θ peak.

25
26 Silica-modified-alumina according to the present invention is preferably
27 prepared by a cogel process. It may be prepared by a variety of methods
28 employing batch and continuous processes in different combinations. The
29 silica-modified-alumina is preferably prepared in accordance with the methods
30 disclosed in commonly assigned U.S. Patent Application Serial
31 No. 10/291,114 titled "Method for Preparing A Highly Homogenous
32 Amorphous Silica-Alumina Composition", filed November 8, 2002 and
33 incorporated by reference herein.

1 The two most important steps in the preparation of a silica-modified alumina
2 cogel are (1) preparation of the clear sol containing silica and alumina and
3 (2) gellation of the sol using a base solution. See U.S. Patent No. 4,289,653,
4 Jaffe and U.S. Patent No. 4,988,659, Pecoraro, both of which are
5 incorporated by reference herein.

6
7 The starting materials for the sol preparation step include aluminum salt, acid,
8 and a silica source. The aluminum salt source that can be used for the
9 synthesis includes aluminum sulfate, aluminum nitrate, aluminum chloride,
10 aluminum bromide, aluminum iodide, aluminum acetate, aluminum alkoxide,
11 aluminum carboxylate, and aluminum metal or alumina dissolved in acid.
12 Feasible acid sources include acetic acid, formic acid, sulfuric acid,
13 hydrochloric acid, and nitric acid. The silicate sources include, but are not
14 limited to, sodium silicate, precipitated silica dissolved in a base, and colloidal
15 silica.

16
17 The sol preparation can be done either via a batch process or a continuous
18 process. It is critical to maintain the pH less than 3.0, preferably less than
19 2.5, and to ensure vigorous and complete mixing of the aluminum salt and
20 silicate solutions to minimize any unwanted gel or particle formation.

21
22 A basic precipitant such as ammonium hydroxide is then added to the
23 acidified sol solution. The addition of the precipitant raises the pH of the sol
24 above 3, resulting in cogelling the silica and alumina species. Dilute ammonia
25 solution is the preferred base for the gellation. In addition to dilute ammonia,
26 other bases such as NaOH, NaAlO₂, KOH or organic amine derivatives can
27 also be used for the gellation. It is preferable to use an inorganic base for its
28 lower cost.

29
30 The gellation step can be done either via batch process or continuous
31 process. The desirable final gellation pH is in the range of 5-9, preferably 6-8.
32 It is critical to have complete, vigorous mixing of the Si-Al solution with the
33 basic precipitant, and to maintain uniform pH throughout the mixture during

1 the precipitant addition step in order to minimize formation of isolated silica
2 domains and alumina domains.

3

4 The precipitated cogel needs to be washed to remove any unreacted silicate
5 and aluminum salt, and then it is ammonium exchanged to remove sodium.
6 The cogel should be aged for approximately 2-5 hours at room temperature or
7 at an elevated temperature of up to about 90°C and the aged cogel may be
8 spray-dried for convenience in handling and storage, or for preparation of
9 support for fluidized bed catalyst. The wet cake may be further processed to
10 the final catalyst from the moist state.

11

12 The preferred method of drying and calcining of spherical form of supports
13 includes an initial spray drying step in an air-purged dryer at 260-450°C and a
14 final calcination at 480-850°C for 0.5-12 hours in a furnace or kiln.

15

16

17 If desired, the material may be extruded to produce a fixed-bed catalyst or
18 catalyst support. The silica-modified alumina as-is or in combination with other
19 ingredients can be formed by adding sufficient amount of water to produce a
20 moisture content of approximately 60% by weight. After mulling for
21 approximately 1 hour, optionally in the presence of peptizing acid or base, the
22 material will attain a plastic or doughy state which is suitable for extrusion in
23 commercial extrusion apparatus. The extrudates then needs to be dried and
24 calcined. The preferred method of drying and calcining includes an initial
25 drying step in an air-purged oven at 65-175°C and a final calcination at
26 480-850°C for 0.5-12 hours in a furnace or kiln. These and other methods of
27 finishing the material are set forth in U.S. Patent No. 4,289,653, Jaffe,
28 incorporated by reference herein.

Examples

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

Example 1: Synthesis of Silica-Modified-Alumina (2.5% SiO₂/ 97.5% Al₂O₃)

An acidic aluminum solution (Solution I containing 10 wt% Al₂O₃) was prepared by dissolving 2309 g of AlCl₃·6H₂O and 13.7 g of hydrochloric acid (37% concentrated) in 2553 g of deionized water. A dilute solution of sodium silicate (Solution II containing 0.30 wt% SiO₂) was prepared by diluting 43.6 g of concentrated sodium silicate solution (contains 29 wt% SiO₂ and 9% Na₂O) with deionized water. The alumina/ hydrochloric acid solution (Solution I) and the silicate solution (Solution II) were pumped separately and simultaneously into the mixing chamber of an in-line blender. Mixing in the in-line blender was vigorous with 1600 RPM blender-blade rotation. The volume of the mixing chamber is smaller than the total volume of solutions pumped in 1 minute (i.e., less than 1 minute residence time per volume). The mixing produced a clear silica and alumina solution at the outlet of the inline blender (Solution III). The pH of the Solution III ranged 1.5 - 1.7. The Solution III contained

Si/Al atomic ratio of 0.022

H⁺/ Na⁺ molar ratio of 1.1

Then the product from the in-line blender (Solution III containing the silica and alumina sol) and the dilute ammonia solution (Solution IV containing 8 wt% NH₃) were pumped separately and simultaneously into the mixing chamber of a second in-line blender for gel formation. The rate of the ammonia solution was adjusted to maintain the pH of the gel product at 7 ± 0.5. The mixing in the in-line blender was again vigorous with 1600 RPM blender-blade rotation. The gel product was collected and then aged at room temperature for 2 hours while stirring. This cogelled silica-modified alumina was filtered to produce a

1 filtered cake. The cake was washed with deionized water followed by an
2 ammonium exchange with a hot solution of ammonium nitrate (8.3 wt%, 24 L.
3 solution) for 15 minutes, and then rinsed with 48 L of deionized water. The
4 final cake was dried at 250°F overnight. The silica-modified alumina was sized
5 to small pieces and calcined under excess dry air at 1000°F for 1 hour for
6 activation. Another sample was calcined at 1200°F for 1 hour to produce
7 material with different porosity. Physical properties of the final silica-modified
8 alumina are summarized in Table 1.

9
10 Example 2: Synthesis of Silica-Modified Alumina (5% SiO₂/ 95% Al₂O₃)

11
12 The preparation procedure of this silica-modified alumina was similar to
13 Example 1. The concentrations of Solution I and Solution II are modified to
14 produce a combined solution of silica and alumina to a composition of

15
16 Si/Al atomic ratio of 0.045

17 H⁺/ Na⁺ molar ratio of 1.1

18
19 Then the product from the in-line blender (Solution III containing the silica and
20 alumina sol) and the dilute ammonia solution (Solution IV containing 8 wt%
21 NH₃) were pumped separately and simultaneously into the mixing chamber of
22 a second in-line blender for gel formation. Then the gel product was purified
23 via ammonium exchange and deionized water rinse. Physical properties of the
24 final silica-modified alumina are summarized in Table 1.

1 Example 3: Synthesis of Silica-Modified Alumina (10% SiO₂/ 90% Al₂O₃)

2

3 The preparation procedure of this silica-modified alumina was similar to
4 Example 1. The concentrations of Solution I and Solution II are modified to
5 produce a combined solution of silica and alumina to a composition of

6

7 Si/Al atomic ratio of 0.094

8 H⁺/ Na⁺ molar ratio of 1.1

9

10 Then the product from the in-line blender (Solution III containing the silica and
11 alumina sol) and the dilute ammonia solution (Solution IV containing 8 wt%
12 NH₃) were pumped separately and simultaneously into the mixing chamber of
13 a second in-line blender for gel formation. Then the gel product was purified
14 via ammonium exchange and deionized water rinse. Physical properties of the
15 final silica-modified alumina are summarized in Table 1.

16

17 Example 4: Commercial Alumina base case (100% Al₂O₃, non-invention)

18

19 Physical properties of commercial pseudoboehmite alumina (Catapal B from
20 Sasol Condea) were compared with the present silica-modified alumina. The
21 pseudoboehmite alumina was calcined under excess dry air at 1000°F for
22 1 hour to convert to the gamma -form of alumina. Another sample was
23 calcined at 1200°F for 1 hour to produce gamma alumina with different
24 porosity. Physical properties of the final gamma alumina are summarized in
25 Table 1.

Table 1

Physical Properties and Conversion Activity
of Silica-Modified Alumina Compositions

	<i>Reference, Gamma Alumina</i>	Silica-Modified Alumina Invention (<i>Example 1</i>)	Silica-Modified Alumina Invention (<i>Example 2</i>)	Silica-Modified Alumina Invention (<i>Example 3</i>)
Nominal SiO ₂ Content, wt%	0	2.5	5	10
<u>Porosity after 1000°F calcinations</u>				
Surface area, m ² /g	293	338	365	412
Total pore volume, cc/g	0.43	0.47	0.44	0.58
<u>Porosity after 1200 °F calcinations</u>				
Surface area, m ² /g	217	293	318	378
Total pore volume, cc/g	0.51	0.48	0.46	0.58
Na, wt%	-	<0.05	<0.05	<0.05
Bulk Si/Al atomic ratio, by elemental anal.	0	0.020	0.041	0.093
Surface Si/Al atomic ratio, by XPS	-	0.013	0.031	0.075
Surface to Bulk Si/Al Ratio	-	0.64	0.75	0.80
XRD, % crystalline alumina phase (38.5° 2θ peak)	100 % (base)	72 %	58 %	59 %
XRD, % linewidth (38.5° 2θ peak)	100 % (base)	163 %	213 %	244 %
<u>nC₆ + iC₆ Model Compound Testing (a)</u>				
Total conversion, wt%	3.1	-	4.7	3.9
nC ₆ conversion, wt%	2.0	-	2.3	1.8
iC ₆ conversion, wt%	4.1	-	7.1	5.9
Isopropylamine TPAD, mmol/g	base	-	Lower than the base	-

(a) Model compound testing was performed at 950°F, 0.68 WHSV of the combined hydrocarbon feed.

The present silica-modified alumina shows excellent physical properties as shown in Table 1. The silica-modified alumina samples show comparable or

1 higher surface area and pore volume than the reference alumina. The present
2 silica-modified alumina shows better resistance to heat treatment in that it
3 maintains the surface area better.

4
5 The bulk Si/Al ratios of the silica-modified alumina samples in Table 1 are
6 nearly identical to the compositions of the synthesis medium (Solution III,
7 combined solution of silica and alumina). This indicates that silica
8 incorporation is stoichiometric, nearly complete incorporation of silica into the
9 alumina structure. The surface Si/Al ratios measured by XPS show
10 comparable values to the bulk Si/Al ratios. The surface-to-bulk Si/Al ratios are
11 close to 1 indicating the Si distribution in the material is uniform and
12 homogeneous.

13
14 Figure 1 compares the powder X-ray diffraction (XRD) pattern of commercial
15 pseudoboehmite alumina to the present homogeneous silica-modified alumina
16 (5 wt% SiO₂ case, Example 2) in dried-only form. The present silica-modified
17 alumina exhibits two distinct characteristics. First, the overall intensity of the
18 X-ray diffraction of the silica-modified-alumina is substantially less than the
19 reference alumina indicating more amorphous nature of the material. By
20 integrating the 38.5 degree 2 θ peak, it has an estimated 58% relative
21 crystallinity compared to the reference alumina. Secondly, the linewidth of
22 each XRD peaks are significantly broader, more than twice, than the
23 reference alumina. By measuring the full-width-at-half-height (FWHH) of the
24 38.5 degree 2 θ peak, it is determined that the linewidth was increased by
25 113% compared to the reference alumina. The other silica-modified alumina
26 samples exhibit the exact same behavior as reported in Table 1. The features
27 of lower relative crystallinity and broader linewidth indicate that the present
28 silica-modified alumina is very homogeneous in nature and the domain size of
29 the alumina crystallites is significantly smaller than the reference alumina
30 (much less than 100 Å).

31
32 All silica-modified-alumina samples showed desirable low activity for
33 hydrocarbon conversion as shown with the model compound testing.

1 Example 2 showed 4.7% total hydrocarbon conversion and
2 Example 3 showed 3.9% conversion, comparable to the reference alumina
3 sample with 3.1% conversion. Temperature programmed amine desorption
4 study also shows that the support acidity of the present silica-modified
5 alumina is comparable to or lower than that of reference gamma alumina. Low
6 acidity of the support is desirable for metal catalyzed reactions where severe
7 isomerization and cracking are undesirable, such as Fischer-Tropsch wax
8 synthesis conditions.

9
10 Example 5: Acid Resistance Test

11
12 A method to obtain cumulative aluminum ion dissolution profile was disclosed
13 U.S. Patent No. 5,733,839 to van Berge et al. in that concentration of
14 aluminum ions was estimated using conductivity measurements at a constant
15 pH as a function of time.

16
17 In the present case, behavior of a support in an acid medium was evaluated
18 by observing a conductivity change in the acid medium using a procedure
19 similar to that disclosed by van Berge et al. For this experiment, 2 g of a
20 support sample, which was calcined earlier at 1350°F for 1 hour, was slurried
21 in a dilute nitric acid solution. Then the conductivity change was monitored for
22 50 - 60 hours while maintaining the slurry pH at 2.0 using an automatic
23 titrator. The conductivity change (Δ) is due to aluminum dissolution to form
24 Al^{3+} and other charged particles in the slurry. Thus the higher conductivity
25 indicates higher dissolution tendency of the support. The conductivity change
26 is plotted as a function time in Figure 2. The figure clearly indicates that
27 silica-modified alumina shows much lower conductivity increase than pure
28 gamma alumina at constant acid consumption, demonstrating the present
29 silica-modified alumina exhibits improved acid resistance.

30
31 While not being bound by any particular theory, the acid resistance of the
32 present homogeneous silica-modified-alumina support may come from very
33 fine domain of alternating silica and alumina phases in the support. The close

1 chemical bonding may generate very effective binding sites for alumina and
2 hydrolyzed aluminum species. Even the digested alumina in the acid medium
3 (partially hydrolyzed colloidal alumina) will be attached to the support with the
4 stronger binding force. As a result, the homogeneous silica-modified-alumina
5 is expected to generate much lower content of "soluble" aluminum species in
6 a catalysis process that contains aqueous medium.

7

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

WHAT IS CLAIMED IS:

1. A homogeneous, amorphous cogel catalyst support comprising a modifying-metal-oxide and a base-metal oxide, wherein the modifying-metal-oxide is homogeneously distributed throughout the base-metal oxide, the catalyst support having a Surface to Bulk modifying-metal /base-metal atomic ratio of from about 0.9 to about 1.1 and exhibiting an X-ray diffraction having broader line width and lower intensity than is exhibited by the base-metal oxide.
2. A catalyst support according to claim 1, wherein the modifying-metal-oxide is selected from the group consisting of silica, titania, zirconia, magnesia and mixtures thereof.
3. A catalyst support according to claim 1, wherein the base-metal-oxide is selected from the group consisting of alumina, silica, titania and mixtures thereof.
4. A catalyst support according to claim 3, wherein the modifying-metal-oxide is selected from the group consisting of silica, titania, zirconia, magnesia and mixtures thereof.
5. A catalyst support according to claim 4, wherein the base-metal oxide is alumina and the modifying-metal-oxide is silica.
6. A catalyst support according to claim 5, wherein the catalyst support comprises from about 70 wt% to about 99.75 wt% alumina.
7. A catalyst support according to claim 5, wherein the catalyst support comprises from about 90 wt% to about 99 wt% alumina.
8. A catalyst support according to claim 5, which has been prepared by a cogel process.

9. A homogeneous, amorphous silica-modified-alumina cogel catalyst support having a Surface to Bulk Si/Al ratio of from about 0.9 to about 1.1 and exhibiting an X-ray diffraction having broader line width and lower intensity than is exhibited by unmodified alumina.
10. A catalyst support according to claim 9, wherein the Surface to Bulk Si/Al ratio is from about 1.0.
11. A catalyst support according to claim 9, wherein the catalyst support comprises from about 70 wt% to about 99.75 wt% alumina.
12. A homogeneous, amorphous silica-modified-alumina catalyst support exhibiting an X-ray diffraction having a broader line width and lower intensity than is exhibited by unmodified alumina.
13. A catalyst support according to claim 12, wherein the full line width is 50% greater than the line width of unmodified alumina when measured at half height.
14. A catalyst support according to claim 12, wherein the intensity is at least 25% lower than for the unmodified alumina.
15. A catalyst for the Fischer-Tropsch process comprising a homogeneous, amorphous cogel catalyst support comprising a modifying- metal-oxide and a base-metal oxide, wherein the modifying-metal-oxide is homogeneously distributed throughout the base-metal oxide, the catalyst support having a Surface to Bulk modifying-metal /base-metal

atomic ratio of from about 0.9 to about 1.1 and exhibiting an X-ray diffraction having broader line width and lower intensity than is exhibited by the base-metal oxide and a catalytically active Group VIII metal.

16. A catalyst according to claim 15, further comprising at least one promoter.
17. A catalyst according to claim 15, wherein the modifying-metal-oxide is selected from the group consisting of silica, titania, zirconia, magnesia and mixtures thereof, the base-metal-oxide is selected from the group consisting of alumina, silica, titania and mixtures thereof.
18. A catalyst according to claim 17, wherein the catalytically active Group VIII metal is selected from the group consisting of cobalt, iron and mixture thereof.