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(57) Abstract

A method of treating a catalyst support comprises introducing onto and/or into an untreated catalyst support which is partially soluble in an aqueous acid solution and/or a neutral aqueous solution, Si, Zr, Cu, Zn, Mn, Ba, Co, Ni and/or La as a modifying component. The modifying component is capable, when present in and/or on the catalyst support, of suppressing the solubility of the catalyst support in the aqueous acid solution and/or the neutral aqueous solution. A protected modified catalyst support which is less soluble or more inert in the aqueous acid solution and/or the neutral aqueous solution, than the untreated catalyst support, is thus formed. A method of forming a catalyst from the modified catalyst support is also provided.

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PROCESS FOR PRODUCING HYDROCARBONS FROM A SYNTHESIS GAS, AND CATALYSTS THEREFOR

THIS INVENTION relates to a process for producing hydrocarbons from a synthesis gas, and to catalysts. It relates in particular to a method of treating a catalyst support to form a modified catalyst support, to a modified catalyst support thus formed, to a method of forming a catalyst from the modified catalyst support, to a catalyst thus obtained, to a process for producing hydrocarbons, and to hydrocarbons thus produced.

According to a first aspect of the invention, there is provided a method of treating a catalyst support, which method comprises introducing onto and/or into an untreated catalyst support which is partially soluble in an aqueous acid solution and/or a neutral aqueous solution, Si, Zr, Cu, Zn, Mn, Ba, Co, Ni and/or La as a modifying component which is capable, when present in and/or on the catalyst support, of suppressing the solubility of the catalyst support in the aqueous acid solution and/or the neutral aqueous solution, thereby to form a protected modified catalyst support which is less soluble or more inert in the aqueous acid solution and/or the neutral aqueous solution, than the untreated catalyst support.

The catalyst support may, in particular, be in particulate form. The modifying component is thus present, in the modified catalyst support particles, on the particle surfaces and/or in internal support frameworks of the particles, ie the modifying component is chemically bonded to the particle surfaces and/or to support frameworks of the particles. For example, the modifying component may be chemically bonded to OH (hydroxy groups) on the support surfaces or via the formation of spinel structures with the support.

In principle, any commercially available catalyst support which is partially soluble in an aqueous acid solution and/or in a neutral aqueous solution, can be used. Examples of untreated catalyst supports that can be used are alumina (Al_2O_3), titania (TiO_2) and magnesia (MgO). When the catalyst support is alumina, any suitable alumina support can, in principle, be used. For example, the alumina support may be that obtainable under the trademark Puralox SCCa 5/150 from CONDEA Chemie GmbH. Puralox SCCa 5/150 (trademark) is a spray-dried alumina support. Similarly, when the catalyst support is titania, any suitable titania support can, in principle, be used. For example, the titania support may be that obtainable under the trademark Degussa P25.

The introduction of the modifying component onto and/or into the catalyst support may include contacting a precursor of the modifying component with the catalyst support, for example, by means of impregnation, precipitation or chemical vapour deposition. Such modifying component precursors include compounds, eg salts or alkoxides, containing the modifying component or elements, viz Si, Zr, Cu, Zn, Mn, Ba, Co, Ni, and/or La.

In one embodiment of the invention, the modifying component precursor may, in particular, be a silicon-based modifying component precursor, eg an organic silicon compound or agent, so that the modifying component is silicon (Si). The organic silicon compound may be tetra ethoxy silane ('TEOS') or tetra methoxy silane ('TMOS').

When a silicon-based modifying component precursor is used with an alumina catalyst support, it may then be used in a quantity such that the silicon level in the resultant protected modified catalyst support is at least 0,06 Si atoms per square nanometer of the untreated or fresh support, preferably at least 0,13 Si atoms per square nanometer of the fresh support, and more preferably at least 0,26 Si atoms per square nanometer of the fresh support.

The upper limit of the modifying component, eg silicon, in the protected modified catalyst support may be set by parameters such as the degree of acidity imparted to the support by the modifying component and/or the porosity of the protected modified catalyst support and/or by the average pore diameter of the protected modified catalyst support. Preferably, the average pore diameter of the protected modified catalyst support as hereinafter described is at least 12nm, as disclosed in South African Patent No. 96/2759, which is hence incorporated herein by reference thereto. Additionally, if an objective is to obtain, from the protected modified catalyst support, a catalyst having a composition of 30g Co/100g Al_2O_3, the untreated Al_2O_3 catalyst support, and also the protected modified catalyst support, must have a pore volume of at least 0,43mℓ/g, as discussed hereinafter with reference to Table 2. The upper limit of the modifying component, eg Si, in the protected modified catalyst support is thus to be selected in such a manner that the geometry, eg the average pore diameter and porosity, of the protected modified catalyst support is not detrimentally effected to an appreciable extent. If the support acidity is negatively influenced by the modifying component, eg as may be the case when silicon is used as the modifying component, then the upper limit of the modifying component in the protected modified support can, instead, be set by the modifying component level at which the support acidity becomes unacceptable.

Thus, when spray-dried Puralox SCCa 5/150 (trademark) alumina is used as the untreated or fresh catalyst support, sufficient silicon-based modifying component precursor is used such that the upper limit of silicon in the resultant protected modified catalyst support is 2,8 Si atoms/nm^2 of fresh catalyst support, preferably 2,5 Si atoms/nm^2 of fresh catalyst support.

Instead, when spray-dried Puralox SCCa 5/150 (trademark) alumina is used as the untreated catalyst support (ie having a surface area of ca 150m^2/g and a pore volume of ca 0,5mℓ/g implying an average pore diameter of ca 13 nm), then the maximum level of silicon may be set in accordance with Table 1.

TABLE 1: Characteristics of silicon modified supports

Silicon level of modified and calcined Al_2O_3 (Si atoms/nm^2 of fresh support)	B.E.T. derived geometries of modified and calcined Al_2O_3		
	Pore volume (mℓ/g)	Surface area (m^2/g)	Average pore diameter (nm)
1	0,48	155	13
2,5	0,48	158	12
2,8	0,44	162	11
7,0	0,39	157	10
14,8	0,25	136	7

The organic silicon compound or agent may be dissolved in an impregnation solvent, which is typically an organic solvent capable of dissolving the silicon compound, such as ethanol, acetone or propanol. The catalyst support may be admixed with the resultant solution to form a treatment mixture. The treatment mixture may be maintained at an elevated temperature for a period of time to impregnate the modifying agent into and/or onto the catalyst support. The elevated temperature may be at or near the boiling point of the impregnation solvent. The impregnation may be effected at atmospheric pressure, and the period of time for which the impregnation is effected may be from 1 minute to 20 hours, preferably from 1 minute to 5 hours. The excess solvent or solution may then be removed, to obtain a modified catalyst support. The removal of the excess solvent or solution may be effected under a vacuum of 0,01 to 1 bar (absolute pressure: hereinafter denoted by (a)), more preferably 0,01 to 0,1 bar (a), and at temperature equal to the boiling point of the solvent, e.g. using known drier equipment, fitted with a mixing device, and of which the jacket temperature is thus higher than the solvent boiling point.

The method may include calcining the silicon-containing modified catalyst support, to obtain the protected modified catalyst support. The calcination of the modified catalyst support may be effected at a temperature from 100°C to 800°C, preferably from 450°C to 550°C, and for a period of from 1 minute to 12 hours, preferably from 1 hour to 4 hours.

Calcination after support modification is necessary to decompose organic groups and to obtain the protected modified support. An optimized calcination time can be obtained by infra-red analysis of the modified support after calcination.

In another embodiment of the invention, the modifying component precursor may be an inorganic cobalt compound so that the modifying component is cobalt (Co). The inorganic cobalt compound, when used, may be cobalt nitrate ($Co(NO_3)_2$).

The inorganic cobalt compound may be dissolved in an impregnation solvent, which is typically water or an organic solvent capable of dissolving the cobalt compound, such as ethanol, acetone or propanol. The catalyst support may be admixed with the resultant solution to form a treatment mixture. The treatment mixture may be maintained at an elevated temperature for a period of time to impregnate the modifying agent into and/or onto the catalyst support. The elevated temperature may be at or near the boiling point of the impregnation solvent. The impregnation may be effected at atmospheric pressure, and the period of time for which the impregnation is effected may be from 1 minute to 20 hours, preferably from 1 minute to 5 hours. The excess solvent or solution may then be removed, to obtain a modified catalyst support. The removal of the excess solvent or solution may be effected under a vacuum, preferably a vacuum of 0,01 to 1 bar(a), more preferably 0,01 to 0,1 bar(a), and at a temperature equal to the boiling point of the solvent, eg using known drier equipment, fitted with a mixing device, and of which the jacket temperature is thus higher than the solvent boiling point.

The method may then include calcining the cobalt-based modified catalyst support, to obtain the protected modified catalyst support. The calcination of the modified catalyst support may be effected at a temperature from 400°C to 900°C, preferably from 600°C to 800°C, and for a period of from 1 minute to 12 hours, preferably from 1 hour to 4 hours to ensure the formation of a relatively water insoluble CoAl spinel layer uniformly covering the total support surface area.

In yet another embodiment of the invention, the modifying component precursor may be an organic zirconium compound so that the modifying component is zirconium (Zr). The contacting of the precursor and the calcination of the modified catalyst support may then be effected in similar fashion to the contacting and calcination hereinbefore described for the cobalt modifying component.

The invention extends to a protected modified catalyst support, when obtained by the method as hereinbefore described.

According to a second aspect of the invention, there is provided a method of forming a catalyst, which method comprises mixing a protected modified catalyst support as hereinbefore described with an aqueous solution of an active catalyst component or its precursor, to form a slurry, and impregnating the protected modified catalyst support with the active catalyst component or its precursor, to form the catalyst.

The active catalyst component precursor may be cobalt nitrate ($Co(NO_3)_2$) so that the active catalyst component in and on the catalyst is cobalt. The support may, as hereinbefore described, be alumina.

The method of forming the catalyst may be in accordance with that described in South Africa Patent No. 96/2759 which is thus incorporated herein by reference. Thus, the mixing of protected modified catalyst support and the active catalyst component or its precursor aqueous solution, and the impregnating, may comprise subjecting a slurry of the catalyst support or carrier, water and the active catalyst component or its precursor to a sub-atmospheric pressure environment, drying the resultant impregnated carrier under a sub-atmospheric pressure environment, and calcining the dried impregnated carrier, to obtain the Fischer-Tropsch catalyst in unreduced form. The unreduced catalyst thus obtained may be washed, eg with water, as also described in ZA 96/2759, to remove unwanted contaminants.

However, the water washing described in ZA 96/2759 can be omitted, under certain conditions. For example, if the following two-stage cobalt slurry phase impregnation and calcination of the active catalyst component precursor, in which the carrier or support is alumina, is followed, then water washing of the resultant catalyst is not required.

Thus, in a first stage or step, if it is assumed that the BET pore volume of the alumina support is x mℓ/g, and that y kg of the support is to be impregnated, the following procedure will ensure proper impregnation:

> (1,82xy)kg $Co(NO_3)_2.6H_2O$ is dissolved in distilled water, aiming for a final volume of >xy, preferably 2xy, litre. This solution is added to a vacuum drier, and heated to a temperature between 60 and 95°C. To this solution, the total inventory of y kg support material is added at atmospheric pressure whilst continuous mixing of the slurry is maintained, eg by means of an internal rotating screw in a conical type vacuum drier. With the gradual application of vacuum, under continuous mixing at a temperature between 60 and 95°C, the loss on ignition (L.O.I.) content of the slurry is reduced (over 3 (or more) hours) from >(136,4x)/ (1+1,86x), preferably (236,4x)/(1+1,86x) mass % to the state of incipient wetness. Loss on ignition (L.O.I.) is defined as the mass % loss observed during complete calcination, ie complete decomposition to Co_3O_4/Al_2O_3. This gradual drying procedure ensures that the cobalt is quantitatively drawn into the pores of the Al_2O_3 support without the occurrence of localized saturation, which results in premature crystallization of cobalt nitrate.
>
> At the state of incipient wetness (L.O.I. of (136,4x)/(1+1,86x)), maximum vacuum (<20 kPa(a)) should be applied whilst ensuring that the bed temperature does not drop below 60°C under continuous mixing. Once the stage of incipient wetness has been reached, vacuum drying should preferably proceed in an uninterrupted fashion, ideally at the conditions:

>60°C (but not higher than 95°C), and a vacuum of <20 kPa(a).

Vacuum drying under these specific conditions should be maintained until a L.O.I. <90% of the L.O.I. value at incipient wetness has been reached.

Direct calcination of this dried material in a fluidized bed, or a rotary kiln, calciner at 200-300°C (ideally 250°C) is then preferably effected.

In a second stage or step, if it is assumed that the BET pore volume of the first stage calcined material is x'mℓ/g, and that y'kg of this material is to be impregnated for a second time, the following procedure will ensure proper impregnation:

A maximum of (1,82x'y') kg $Co(NO_3)_2.6H_2O$ can be added during this second impregnation, but this may exceed the aimed for cobalt loading of the catalyst. Table 2 provides the correlation between the pore volume of the starting Al_2O_3 (ie x mℓ/g), and the maximum attainable cobalt loading to be associated with a two-step impregnation procedure:

TABLE 2

Pore volume of starting support material (mℓ/g)	Maximum attainable cobalt catalyst loading during a catalyst preparation which is limited to 2 impregnation steps
0,50	35,5g Co/100g Al_2O_3
0,49	34,7g Co/100g Al_2O_3
0,48	33,9g Co/100g Al_2O_3
0,47	33,1g Co/100g Al_2O_3
0,46	32,4g Co/100g Al_2O_3
0,45	31,6g Co/100g Al_2O_3
0,44	30,8g Co/100g Al_2O_3
0,43	30,1g Co/100g Al_2O_3
0,42	29,3g Co/100g Al_2O_3
0,41	28,6g Co/100g Al_2O_3
0,40	27,8g Co/100g Al_2O_3

If the objective is a final catalyst of composition 30g Co/100g Al_2O_3, the starting Al_2O_3 support must have a pore volume ≥0,43mℓ/g. If, however, the pore volume is larger than 0,43mℓ/g, the estimated amount of (1,82x'y')kg $Co(NO_3)_2.6H_2O$ should be adjusted in order to ensure the desired catalyst composition. This amount of $Co(NO_3)_2.6H_2O$ is dissolved in distilled water aiming for a final volume of >x'y', preferably 2x'y', litre. This solution is added to a vacuum drier, and heated to a temperature between 60 and 95°C. To this solution, the final inventory of y' kg of the first stage material is added at atmospheric pressure, whilst continuous mixing of the slurry is maintained, eg by means of an internal rotating screw in a conical type vacuum drier. With the gradual application of vacuum, under continuous mixing at a temperature between 60 and 95°C, the L.O.I. content of the slurry is reduced (over 3 or more hours) to the state of incipient wetness. As stated hereinbefore, this gradual drying procedure ensures that the cobalt is quantitatively drawn into the pores of the support material without the occurrence of localized saturation, which results in premature crystallization of cobalt nitrate.

At the stage of incipient wetness, maximum vacuum (<20kPa(a)) should be applied whilst simultaneously ensuring that the bed temperature does not drop below 60°C under continuous mixing. Once the stage of incipient wetness has been reached, vacuum drying should proceed in an uninterrupted fashion, ideally at the conditions:

>60°C (but not higher than 95°C),
and a vacuum of <20kPa(a)

Vacuum drying under these specific conditions should be maintained until a L.O.I. <90% of the L.O.I. value at incipient wetness has been reached.

Direct calcination of this dried material in a fluidized bed, or a rotary kiln, calciner at 200-300°C (ideally 250°C) is then preferably effected.

During either, or both, of the two abovementioned slurry phase cobalt impregnation steps, a water soluble precursor salt of Pt or Pd may be added, as a dopant capable of enhancing the reducibility of the active component. The mass proportion of this dopant, when used, to cobalt may be between 0,01:100 and 0,3:100.

The invention extends also to a catalyst, when obtained by the method as hereinbefore described.

This catalyst is thus in unreduced form, and requires reduction or activation before it can be used. This may be effected by subjecting it to heat treatment under the influence of a reducing gas such as hydrogen.

According to a third aspect of the invention, there is provided a process for producing hydrocarbons, which includes contacting a synthesis gas comprising hydrogen (H_2) and carbon monoxide (CO) at an elevated temperature between 180°C and 250°C and an elevated pressure between 10 and 40 bar with a catalyst as hereinbefore described, after activation or reduction thereof, to obtain hydrocarbons, by means of a slurry phase Fischer-Tropsch reaction of the hydrogen with the carbon monoxide.

The invention extends also to hydrocarbons, when produced by the process as hereinbefore described.

It is known that an alumina supported cobalt based slurry phase Fischer-Tropsch catalyst produces a wax product when used in a Fischer-Tropsch reaction of a synthesis gas, comprising hydrogen and carbon monoxide.

Such catalysts have hitherto preferably been produced by slurry impregnation of an alumina support using an aqueous cobalt nitrate precursor solution, of which the pH can vary between 1 and 6. The alumina support partially dissolves in aqueous acid, as well as neutral aqueous solutions. After dissolution the aluminium ions can, in the presence of cobalt ions, re-precipitate as hydrotalcite-like structures, eg $Co_6Al_2CO_3(OH)_{16}.4H_2O$. These amorphous hydrotalcite-like structures are physically adsorbed and loosely bonded to the original alumina surface. The formation of irregular structures on the surfaces of supports present after impregnation of, respectively, alumina with an aqueous nickel nitrate solution, magnesia with an aqueous ruthenium chloride solution and titania with an aqueous platinum chloride solution is also found. This phenomenon is thus not limited to alumina (Al_2O_3), but can also be found when using alternative supports such as magnesia (MgO) and titania (TiO_2).

A serious problem that can arise when such catalysts, which are thus prepared on untreated supports, are used, as observed during larger scale pilot plant synthesis runs, is the undesired high cobalt content of the wax product. Commercialisation of the slurry phase Fischer-Tropsch synthesis process, using the known untreated alumina supported cobalt catalyst, can result in the wax product containing more than 50ppm cobalt, after filtration through a Whatmans 42 (trademark) filter paper (hereinafter referred to as "the filtered wax product" or "the filtered wax"). During slurry impregnation of an untreated alumina support, using an aqueous cobalt nitrate solution, cobalt nitrate will deposit on the loosely bonded hydrotalcite-like structures. These cobalt on loosely bonded hydrotalcite-like structures can dislodge during extended runs and contaminate the wax product with cobalt rich ultra fines. These fines, of submicron nature, exit the reactor in the waxy hydrocarbon product. Due to the high cost of cobalt, this is a highly undesirable problem which has thus been solved, or at least alleviated, with this invention. Said alumina support should thus be protected during aqueous slurry impregnation by improving the inertness of the alumina surface, to prevent formation of cobalt ultra fines during Fischer-Tropsch synthesis. This is achieved in the present invention.

The invention will now be described in more detail with reference to the following non-limiting examples and with reference to the drawings.

In the drawings

FIGURE 1 shows dissolution profiles for a pure or unmodified alumina support, and silica modified alumina supports according to the invention;

FIGURE 2 shows dissolution profiles for an unmodified alumina support, illustrating the influence of solids concentrations;

FIGURE 3 shows a parity plot of percentage carbon atom C_{19+} selectivities of a 20 mass % cobalt supported catalyst prepared on a Si modified alumina support (surface concentration of 2,5 Si atoms per nm^2 support) and its unmodified alumina supported equivalent;

FIGURE 4 shows the cobalt content of filtered waxes, produced on Pilot Plant scale, using supported cobalt catalysts obtained from unmodified alumina supports, and silica modified alumina supports according to the invention;

FIGURE 5 shows the cobalt content of filtered waxes produced on Works Pilot Plant scale using supported cobalt catalysts obtained from unmodified alumina as well as silica modified alumina in accordance with the invention;

FIGURE 6 shows dissolution profiles for an unmodified alumina support, and a cobalt modified support according to the invention;

FIGURE 7 shows dissolution profiles for a pure or unmodified titania support, and silica modified titania supports according to the invention;

FIGURE 8 shows dissolution profiles for a pure or unmodified alumina support, and silica modified alumina supports according to the invention;

FIGURE 9 shows the cobalt content of filtered waxes produced on Pilot Plant scale using supported cobalt catalysts obtained from unmodified alumina as well as from silica modified alumina in accordance with the invention;

FIGURE 10 shows dissolution profiles for a pure alumina support, and a zirconium modified alumina support according to the invention;

FIGURE 11 shows dissolution profiles for different alumina crystal phases; and

FIGURE 12 shows a plot of relative support acidity against silicon content of alumina.

EXAMPLE 1

1.1 Modification of alumina support

A spray-dried Puralox SCCa 5/150 (trademark) alumina support, in the form of spherical particles, obtainable from Condea Chemie GmbH of Überseering 40, 22297, Hamburg, Germany, was used. The surfaces of the support particles were modified with silicon. An impregnation method was used to achieve the modification. Thus, silicon, in the form of TEOS (tetra ethoxy silane) as precursor, was added to ethanol at 60°C, which was thus used as an impregnation solvent. The particulate alumina support was added to this solution, which was then kept at 50°C-75°C for 1 hour. Subsequently, the solvent was removed under vacuum at 29,5-88,8kPa(a), with a jacket temperature of the drier equipment of 95°C. The resultant modified support, in particulate form, was then calcined at 500°C for 2 hours, to obtain a particulate protected modified catalyst support. Any volatile organic solvent can, in principle, be used provided that TEOS is soluble therein.

A maximum of 2,5 atoms Si/nm^2 alumina can be added in one impregnation step using ethanol as impregnation solvent. Acetone can instead be used as solvent. The silica level can be increased by multiple impregnation steps. However, higher levels of silica due to multiple impregnations could lead to multi layers of silica, changing the geometry and/or chemical reactivity of the catalyst support.

Calcination after support modification is necessary to decompose the organic groups and to obtain the protected silicon modified alumina support, through dehydration of the resultant $AlOSi[OH]_3$ species. Infra-red analysis of the modified support after 1, 2 and 12 hours of calcination showed that the methyl and ethyl peaks of the ethoxy groups disappeared after 2 hours of calcination. The optimized calcination time is, therefore, 2 hours.

The addition of silica did not detrimentally alter the geometry of the alumina support. The pore volume and surface area of the untreated alumina support were:

Surface area: 150m^2/g
Pore volume: 0,50mℓ/g

The support geometry is important with respect to Fischer-Tropsch synthesis performance of the resultant catalyst based thereon, to obtain a desired activity and/or selectivity without the use of synthesis enhancing promoters eg the carrier preferably has a specific minimum pore size, eg a pore size of at least 12 nm.

1.2 Conductivity measurements

Alumina dissolves in an aqueous medium at low pH. The dissolution of alumina results in the formation of aluminium ions. As more alumina dissolves, the concentration of aluminium ions increases with time. The increase of aluminium ions with time was followed by monitoring the conductivity at a constant pH of 2. The pH was kept constant by automated addition of a 10% nitric acid solution. The results are set out in Figures 1 and 8.

In Figures 1 and 8, the cumulative mg Al dissolved per m^2 fresh support were plotted against time. It can be seen that the unprotected pure alumina dissolves faster than the protected silicon modified alumina. Moreover, a higher level of silica provides better protection against aqueous/acid attack, ie the support modified by 4,3 Si atoms/nm^2 fresh alumina exhibits the highest suppression of alumina dissolution. Solid concentrations do not seem to exert a significant influence on the dissolution profile, as shown in Figure 2.

1.3 TEM experiments

Cobalt based alumina supported catalysts were prepared on the modified alumina supports of 1.1, using the method described in Example 60 of ZA 96/2759. The presence of an amorphous hydrotalcite-like layer was investigated by High Resolution Scanning Electron Microscopy (HRSEM), and Transmission Electron Microscopy (TEM). TEM micrographs identified the presence of an amorphous layer in samples prepared with unmodified alumina supports. Sub-micron pure boehmite star-like crystals were also observed in these samples, thus confirming dissolution followed by recrystallisation. During slurry impregnation of the catalyst support to obtain the resultant cobalt based catalyst, the active phase (cobalt) will deposit on the physically bonded hydrotalcite-like structures. This active cobalt phase, deposited on the physically bonded hydrotalcite layer, may dislodge during Fischer-Tropsch synthesis and contaminate the wax product with active phase-containing ultra fines. These amorphous layers and the star-like crystals are not present in catalysts prepared on the modified alumina supports. Hence, formation of active phase ultra fines, when using catalysts prepared using the modified supports of the invention, are at least minimized. The amorphous layer is not specific for alumina, but has also previously been found in TiO_2 and MgO supported catalysts. In all three cases, the amorphous layers were physically bonded to the support, with the subsequent catalyst preparation steps, ie calcination and/or reduction, unlikely to provide sufficiently high temperature to achieve recrystallization into, eg spinels.

1.4 Fischer-Tropsch synthesis tests

It would have been expected that the incorporation of silicon into the alumina framework might influence the acidity of the resultant support and could negatively influence the hydrocarbon product selectivity during Fischer-Tropsch synthesis utilizing a catalyst prepared on such supports. However, to prevent the undue introduction of surface acidity of the alumina support, after TEOS impregnation, the modified support was only calcined at <700°C, preferably at 500°C, to remove the organic groups and dehydrate the support without significant incorporation of Si into the Al_2O_3 framework, at which temperature it is believed that negligible zeolite type surface acidity will result.

1.5 Laboratory slurry phase Fischer-Tropsch synthesis tests:

Between 10 and 30g properly externally reduced catalyst, prepared on preshaped spray-dried modified or unmodified support, ranging between 38μm to 150μm, was suspended in 300mℓ molten wax and loaded in a CSTR with an internal volume of 500mℓ. The feed gas consisted of hydrogen and carbon monoxide in a H_2/CO molar ratio from 1,5/1 to 2,3/1. This reactor was electrically heated and sufficiently high stirrer speeds were employed so as to eliminate any gas-liquid mass transfer limitations. The feed flow was controlled by means of Brooks mass flow controllers, and space velocities ranging from 2 and 4 $m^3{}_n$/(h.kg catalyst) were used. GC analyses of the permanent gases as well as the volatile overhead hydrocarbons were used in order to characterize the product spectra.

All catalysts were prepared according to the procedure described for Example 60 of ZA 96/2759 and reduced, prior to synthesis, in a tubular reactor at a pure hydrogen space velocity of 2500h^{-1} and atmospheric pressure. The temperature was increased from room temperature to 350°C to 425°C at a rate of 1°C/min, after which isothermal conditions were maintained for 6 to 16 hours. The results are given in Tables 3 and 4.

TABLE 3: Laboratory CSTR Fischer-Tropsch synthesis performance comparison between catalysts prepared on unmodified, 1,0 Si atom/nm^2 and 2,2 Si atoms/nm^2 Al_2O_3 modified supports

	2.2 Si atoms/nm^2 Al_2O_3	1,0 Si atom/nm^2 Al_2O_3	Unmodified alumina
Synthesis conditions			
Calcined catalyst mass (g)	21,5	24,2	23,3
Reactor temperature (°C)	220	219,6	220,4
Reactor pressure (bar)	20	19,9	20,6
Time on stream (h)	20	22	15
Feed gas composition:			
H_2(vol%)	50,1	55,5	51,2
CO(vol%)	26,9	24,1	28,0
CO_2(vol%)	0,4	0,4	0,5
Syngas (H_2+CO) space velocity ($m^3{}_n$/kg cat/h)	2,2	3,0	2,2
Rector partial pressures:			
H_2(bar)	3,4	4,8	3,7
CO(bar)	1,9	2,4	2,5
H_2O(bar)	5,5	4,7	5,6
CO_2(bar)	0,3	0,2	0,4
Synthesis performance			
Conversions: %CO	76,1	66,7	70,9
%syngas	76,4	70,1	74,5
Productivity (kg HC/kg cat/h)	0,358	0,433	0,343
Relative intrinsic specific Fischer-Tropsch activity	1,04	1,08	1,00
% C-atom CH_4 selectivity	6,6	6,7	4,4
%CO of total amount of CO converted to CO_2	3,9	1,8	4,3

During the laboratory CSTR Fischer-Tropsch slurry phase synthesis runs reported in Table 3, prepared on either unmodified or on silica modified alumina, the filtered wax produced remained white and the cobalt content was below the detection limit (<1ppm).

Having applied a reported cobalt based Fischer-Tropsch kinetic equation, such as:

$$r_{FT} = (k_{FT}P_{H2}P_{CO})/(1 + \beta\ P_{CO})^2$$

the Arrhenius derived pre-exponential factor of k_{FT} was estimated for each of the 3 reported runs. By defining the relative intrinsic specific Fischer-Tropsch activity as (pre-exponential factor of Si modified catalyst)/(pre-exponential factor of the unmodified catalyst), it can be concluded that support modification did not affect the intrinsic activities.

Table 4: Laboratory CSTR Fischer-Tropsch reactor wax (i.e. C_{19+}) selectivity comparison between catalysts prepared on an unmodified and a modified alumina of composition 2,2 Si atoms/nm^2 of fresh support

Synthesis conditions								Estimated C_{19+} mass % selectivities	
Temp (°C)	Pressure (bar)	Feed Composition (vol %)		Syngas space velocity (m^3_n/kg cat.h)	Reactor partial pressures (bar)			Measured for a 2,2 Si atoms/nm^2 support prepared catalyst	Model prediction for a unmodified support prepared catalyst
		H_2	CO		H_2	CO	H_2O		
219	20,0	41,9	26,6	2,46	4,6	4,0	2,4	53,9	52,8
231	20,2	43,4	27,6	3,70	4,2	3,9	3,1	44,8	53,6
231	20,3	43,1	26,6	3,75	4,1	3,6	3,1	48,2	50,4
231	20,5	38,7	17,8	2,03	2,2	1,1	3,3	22,6	11,2
231	20,5	39,3	17,4	2,09	2,4	1,1	3,6	23,4	10,0
231	20,9	55,4	25,9	3,35	5,0	2,4	5,4	38,5	26,1
231	21,0	43,8	21,7	3,40	4,2	2,2	3,6	42,2	25,9
230	19,9	49,8	32,6	3,88	6,0	5,1	3,1	51,9	58,2
230	19,5	52,0	27,3	2,19	3,5	2,5	5,2	39,9	36,2
230	19,8	49,9	25,0	2,23	4,6	2,5	4,1	36,3	29,7

A graphical illustration of Table 4 is presented in Figure 3 indicating that at conditions favouring high molecular weight selectivities, it could be concluded that the catalyst prepared on a Si modified support does under achieve somewhat.

During a confidential Pilot Plant Fischer-Tropsch synthesis test run, using 5 kg of catalyst prepared on unmodified alumina, in a 11m high bubble column slurry reactor (ie Pilot Plant scale) with an external recycle, the filtered wax product turned grey after about 10 days on line and the cobalt content increased to 350ppm after 25 days on line, as shown in Figure 4.

A similar observation was made during a confidential test run, in a 25m high bubble column slurry reactor (ie Works Pilot Plant scale) with sufficient backmixing to ensure a uniform catalyst suspension, using 1500 kg of catalyst prepared on unmodified alumina, as shown in Figure 5.

In both these Pilot Plant reactors, the mechanical stress on the catalyst is significantly more severe than in the laboratory CSTR reactor.

The presence of a high cobalt content in the wax product is believed to be due to the dislodgement of cobalt crystallites deposited on top of the physically bonded cobalt containing hydrotalcite-like structures, present in the catalyst after aqueous slurry impregnation, when the catalyst is prepared from an unmodified support.

Pilot Plant synthesis test runs with catalysts prepared on 1,0 Si atoms/nm^2 Al_2O_3 and 2,2 Si atoms/nm^2 Al_2O_3 modified alumina support showed a substantial improvement with respect to the submicron cobalt particulate contamination in the filtered wax product. After 70 days on line the catalyst with 2 Si atom/nm^2 Al_2O_3 did not show any cobalt in the filtered wax product (Figure 4). A test run in the Works Pilot Plant bubble column slurry reactor with 1000 kg of catalyst prepared on 1,0 Si atoms/nm^2 Al_2O_3 modified alumina support also showed a dramatic improvement in the cobalt content in the wax product compared to the run with the catalyst on the unmodified support (Figure 5). The cobalt content in the wax product was on average between 5 and 10ppm.

From the Works Pilot Plant synthesis tests, it can be seen that the improvement of the inertness of the alumina support by modifying it with silica, as was shown by TEM and conductivity measurements, also prevented the dislodging of ultra fine cobalt rich particulates during slurry phase Fischer-Tropsch synthesis.

EXAMPLE 2

2.1 Modification of alumina support

Cobalt, in the form of cobalt nitrate as precursor, was added to acetone at 45°C. Acetone was thus used as an impregnation solvent. A particulate alumina support was added to this solution, and the resultant mixture kept at 60°C for 10 minutes. The solvent was then removed under a vacuum of 3 kPa(a) with a jacket temperature of the drier equipment at 95°C. The resultant modified support was subsequently calcined at 800°C for 2 hours to obtain a protected modified catalyst support.

The high calcination temperature was aimed at obtaining a spinel-type protected modified support.

In Figure 6, the dissolution profiles for untreated and cobalt modified alumina supports, in accordance with this Example, are plotted. Figure 6 shows that modification of the untreated alumina support with cobalt, increased the resistance to dissolution.

The addition of cobalt had a small effect on the geometry of the support:

Before modification:	Surface area:	155 m^2/g
	Pore volume:	0,48 cc/g
After modification:	Surface area:	154 m^2/g
	Pore volume:	0,43 cc/g

EXAMPLE 3

3.1 Modification of titania support

Particulate titanium dioxide (Degussa P25 (trademark)) support was calcined at 650°C for 16 hours, spray dried and classified to 75-150 micron. The support had a rutile content of 80% and a surface area of $27m^2/g$.

This support was also modified in the same fashion as described in Example 1 by addition of TEOS and calcination at 500°C. The silicon content was analyzed as 4,5 Si atoms/nm^2 fresh support.

Titania dissolves in an aqueous acid medium. The dissolution of titania results in the formation of titanium ions. The increase of titanium ions with time was followed by monitoring the conductivity at a constant pH of 2. The pH was kept constant by automated addition of a 10% nitric acid solution.

In Figure 7, the dissolution profiles of titania are plotted. This indicated that modification of the pure titania did bring along an increase in resistance to dissolution.

EXAMPLE 4

A Puralox 5/150 alumina support surface was modified with silicon. The method of Beguin B Garbowski E and Primet M, J. Catal. 1991, 127, 595 was used as background for the silicon modification or impregnation method. Silicon, using TEOS (tetra ethoxy silane) as modifying component precursor, was added to ethanol at 50-75°C which was thus used as an impregnation solvent. Alumina was added to this solution, which was then kept at 50-75°C for 1 hour. Subsequently, the solvent was removed under vacuum at 29,5-88,8 kPa(a) with a jacket temperature of the drier equipment of 95°C. The modified support obtained was then calcined at 500°C for 2 hours. Any organic solvent can be used as long as TEOS is soluble in it.

The amount of precursor was such that the final silicon level was 0,26 Si atoms/nm^2 of fresh alumina support.

EXAMPLE 5

A modified support was prepared in the same way as in Example 4 except that the amount of precursor added was such that the final silicon level was 1,0 Si atoms/nm^2 of fresh alumina support.

EXAMPLE 6

A modified support was prepared in the same way as Example 4 except that the amount of precursor added was such that the final silicon level was 2,0 Si atoms/nm^2 of fresh alumina support.

EXAMPLE 7 - Conductivity Measurements

Figure 8 shows that the dissolution of alumina is also suppressed by the introduction of relatively small quantities of silicon. Levels as low as 0,26 Si atoms/nm^2 of fresh alumina support offer protection against dissolution, with increasing protection as the silicon level increases.

EXAMPLE 8

Silicon levels of 2,5 atoms/nm^2 of fresh alumina support were found to be the maximum attainable level to be achieved via a single impregnation step as per Example 1. Silicon levels of 2,8 Si atoms/nm^2 fresh support, 4,3 Si atoms/nm^2 fresh support, 7,0 Si atoms/nm^2 fresh support and 14,8 Si atoms/nm^2 fresh support were prepared as described in Example 4 with the exception that multiple impregnation steps were employed with a 500°C for 2 hours calcination treatment after each consecutive impregnation step.

EXAMPLE 9 - Fischer-Tropsch Synthesis Test

A pilot plant batch (ca 30kg) of catalyst was prepared on a particulate alumina support which had been modified with the lowest silicon level, ie 0,26 Si atoms/nm^2 of fresh alumina support. This catalyst was tested during a confidential pilot plant Fischer-Tropsch synthesis run in a 11m high bubble column reactor with an external recycle. Figure 9 shows a comparison of the cobalt content in the secondary filtered wax between this run and a run performed using a catalyst on an unmodified support. No cobalt was shown in the filtered wax product of the modified catalyst.

Thus a level of 0,26 Si atoms/nm^2 of alumina support successfully suppressed the dissolution characteristics to such an extent that the formation of cobalt rich ultrafine particulate material during slurry phase Fischer-Tropsch synthesis was successfully suppressed.

EXAMPLE 10

Zirconium, in the form of zirconium isopropoxide, was added under an inert atmosphere to isopropanol. Isopropanol was thus used as the impregnation solvent. A particulate alumina support was added to this solution, and the mixture stirred at 60°C for 1 hour. The solvent was then removed under a vacuum of 3kPa(a) with a jacket temperature of the drier equipment at 95°C. The resultant modified support was subsequently calcined at 600°C for 2 hours to obtain a protected modified catalyst support. The amount of modifying component was found to be 0,1 Zr atoms per square nanometer fresh support.

In Figure 10, the dissolution profile of the fresh Condea Puralox SCCa 5/150 (trademark) alumina support is plotted against the dissolution profile of the zirconium modified alumina support described above. The addition of zirconium to the fresh support thus improved the resistance of the support to dissolution and aqueous/acid attack.

EXAMPLE 11

Dissolution profiles of different alumina crystal phases were determined and compared to the commercially available Condea Puralox SCCa 5/150 (trademark) alumina support, which was used in, for example, Example 1. The results are given in Figure 10.

The crystal phases that were tested, were delta, gamma and alpha alumina. The pure aluminas were prepared by calcination of the raw alumina material boehmite or $Al(OH)_3$ at different temperatures; gamma alumina being obtained at the lowest calcination temperature between 500°C to 700°C, followed by delta alumina at a calcination temperature of 850°C, and alpha alumina at a calcination temperature of 1150°C.

The surface area of these supports is greatly affected by the calcination temperature. Thus, a support, which contains mostly gamma alumina, will have the highest surface area, which is desirable in heterogeneous catalysis. The gamma alumina support, however, exhibited a higher dissolution behaviour after 30 hours compared to delta and alpha alumina. It is known that OH groups present on the surface of an alumina support can act as initiators for aluminium extraction and therefore dissolution. Calcination of alumina at high temperatures causes dehydration of the support and therefor loss of surface hydroxyl groups.

Thus, from Figure 11, it is clear that delta alumina has a lower dissolution profile than gamma alumina, while alpha alumina has a lower dissolution profile than delta alumina. It can therefore be concluded that an alumina Fischer-Tropsch catalyst support, which mainly consists of a mixture of delta and gamma alumina, such as, for example, Condea Puralox SCCa 5/150 (trademark) alumina support would be susceptible to aqueous/acid attack and subsequent dissolution.

EXAMPLE 12

The acidity of a Fischer-Tropsch catalyst support plays an important role in the selectivity of said catalyst under Fischer-Tropsch synthesis conditions. By modifying the support with silica, as shown in Example 1, the support acidity can possibly be influenced negatively. A test reaction can determine whether the support's acidity or basicity is influenced.

The dehydration reaction rate of isopropanol over a catalyst gives a relative indication of the acidity of the catalyst:

$$CH_3CH(OH)CH_3 \xrightarrow[\text{Acidity}]{} CH_2{=}CHCH_3 + H_2O$$

$$\text{Catalyst Acidity}$$

By measuring the propylene formation rate over different supports, their relative acidity can be compared.

Silica was impregnated at four different levels onto a Condea Puralox SCCa 5/150 (trademark) alumina support by using TEOS as silica source, as detailed in Example 1. After impregnation, the supports were calcined at 500°C. The silica levels were 2,5, 3,5, 8,5 and 15,6 Si atoms/nm^2 fresh support respectively.

Test procedure:

In each test run, 3,5g of the modified support was loaded into a micro fixed bed reactor. The modified support was heated to 195°C under hydrogen flow at atmospheric pressure. After the temperature had stabilized at 195°C, isopropanol was co-fed to the reactor at a fixed liquid flow rate of 30g/h, whilst the H_2 flow was maintained at $12\ell_n$/h. An online GC was used to analyze the reaction products after 15 minutes online. The relative support acidity of modified support Z is defined as: (observed propylene formation rate of support Z)/(observed propylene formation rate of the fresh support), with the rates being expressed per unit surface area.

Figure 12 clearly indicates that the acidity of the silicon modified supports sharply increases at a level exceeding 2,5 Si atoms/nm^2 of fresh alumina support. Seeing, however, that an upper silicon modification level of 2,5 Si atoms/nm^2 fresh alumina support is also the preferred upper Si level from a geometry influencing point of view, both of these upper Si level controlling criteria can successfully be met simultaneously.

The Inventors have thus developed a catalyst impregnated on a modified catalyst support with excellent Fischer-Tropsch synthesis behaviour, resulting in high activity and selectivity. It was surprisingly found that an increased support inertness towards an acidic aqueous attack during slurry phase impregnations, resulted in a dramatic decrease in the formation of active phase containing ultra-fines during slurry phase Fischer-Tropsch synthesis. A slurry phase Fischer-Tropsch process, using the modified supported catalyst, will thus result in a wax product containing less than 50ppm active phase ultra fines throughout extended synthesis runs, thus reducing the cost for the catalyst used in the slurry phase Fischer-Tropsch process substantially. The problem of removing solids from the simplified due to the extreme difficulty with which separation of submicron particulates from this liquid product is achieved.

CLAIMS:

1. A method of treating a catalyst support, which method comprises introducing onto and/or into an untreated catalyst support which is partially soluble in an aqueous acid solution and/or a neutral aqueous solution, Si, Zr, Cu, Zn, Mn, Ba, Co, Ni and/or La as a modifying component which is capable, when present in and/or on the catalyst support, of suppressing the solubility of the catalyst support in the aqueous acid solution and/or the neutral aqueous solution, thereby to form a protected modified catalyst support which is less soluble or more inert in the aqueous acid solution and/or the neutral aqueous solution, than the untreated catalyst support.

2. A method according to Claim 1, wherein the catalyst support is in particulate form, with the modifying component being present, in the modified catalyst support particles, on the particle surfaces and/or in internal support frameworks of the particles by being chemically bonded to hydroxy groups on the support surfaces or through the formation of spinel structures with the support.

3. A method according to Claim 2, wherein the untreated catalyst support is alumina, titania or magnesia, and wherein the introduction of the modifying component onto and/or into the catalyst support includes contacting a precursor of the modifying component with the catalyst support, and thereafter calcining the modifying component-containing modified catalyst support, to obtain the protected modified catalyst support.

4. A method according to Claim 3, wherein the contacting of the precursor with the catalyst support includes dissolving the precursor in an impregnation

solvent; admixing the particulate catalyst support with the resultant solution to form a treatment mixture; maintaining the treatment mixture at an elevated temperature at or near the boiling point of the impregnation solvent and at about atmospheric pressure, for from 1 minute to 20 hours; and removing excess solvent or solution under a vacuum of 0,01 to 1 bar(a) to obtain the modified catalyst support, and wherein the calcination of the modified catalyst support is effected at a temperature from 100°C to 800°C and for a period of from 1 minute to 12 hours.

5. A method according to Claim 4, wherein a silicon-based modifying component precursor is used so that the modifying component is Si, with the untreated catalyst support being alumina, and with the precursor being used in a quantity such that the silicon level in the resultant protected modified catalyst support is at least 0,06 Si atoms per square nanometer of the untreated or fresh support.

6. A method according to Claim 5, wherein the untreated support is spray-dried Puralox SCCa 5/150 (trademark) and wherein the precursor is used in a quantity such that the silicon level in the resultant protected modified catalyst support is not more than 2,8 Si atoms/nm^2 of fresh catalyst support.

7. A method according to Claim 4, wherein an inorganic cobalt compound is used as the modifying component precursor, so that the modifying component is Co.

8. A method according to Claim 4, wherein an organic zirconium compound is used as the modifying component precursor, so that the modifying component is Zr.

9. A protected modified catalyst support, when obtained by the method of any one of Claims 1 to 8 inclusive.

10. A method of forming a catalyst, which method comprises mixing a protected modified catalyst support according to Claim 9 with an aqueous solution of an active catalyst component or its precursor, to form a slurry, and impregnating the protected modified catalyst support with the active catalyst component or its precursor, to form the catalyst.

11. A method according to Claim 10, wherein the active catalyst component precursor is cobalt nitrate so that the active catalyst component in and on the catalyst is cobalt.

12. A method according to Claim 11, wherein the mixing of the protected modified catalyst support and the active catalyst component or its precursor aqueous solution, and the impregnating, comprises subjecting a slurry of the catalyst support or carrier, water and the active catalyst component or its precursor to a sub-atmospheric pressure environment, drying the resultant impregnated carrier under a sub-atmospheric pressure environment, calcining the dried impregnated carrier, to obtain the catalyst in unreduced form, and washing the unreduced catalyst with water.

13. A method according to Claim 11, wherein the support is alumina, and wherein the following two-stage cobalt slurry phase impregnation and calcination of the active catalyst component precursor is effected:

in a first stage or step, (1,82xy)kg $Co(NO_3)_2.6H_20$, where x is the BET pore volume of the alumina in mℓ/g and y is the total mass of the support to be impregnated in kg, is dissolved <u>in</u> sufficient distilled water such that the final volume of the solution is $>xy$ litre; this solution is heated to a temperature between 60 and 95°C; to this solution is added the total inventory of y kg support material at atmospheric pressure whilst continuous mixing of the slurry is maintained; with the gradual application of vacuum, under continuous mixing at a temperature between 60 and 95°C, the loss on ignition (L.O.I.) content of the slurry is reduced, over 3 or more hours, from $>(136{,}4x)/(1+1{,}86x)$ mass % to a state of incipient wetness, with loss on ignition (L.O.I.) being defined as the mass % loss observed during complete calcination or complete decomposition to Co_3O_4/Al_2O_3; at the state of incipient wetness (L.O.I. of $(136{,}4x)/(1+1{,}86x)$), a vacuum of <20 kPa(a) is applied whilst ensuring that the temperature does not drop below 60°C under continuous mixing; once the state of incipient wetness has been reached, vacuum drying is proceeded with in an uninterrupted fashion, at the conditions: temperature >60°C, but not higher than 95°C, and a vacuum of <20 kPa(a); vacuum drying under these specific conditions is maintained until a L.O.I. <90% of the L.O.I. value at incipient wetness has been reached; direct calcination of this dried material at 200°C to 300°C is then effected; and thereafter

in the second stage or step, it is assumed that the BET pore volume of the first stage material is x'mℓ/g, and that y'kg of this material is to be impregnated for a second time, and the following procedure is adapted for proper impregnation:

a maximum of $(1{,}82x'y')$ kg $Co(NO_3)_2.6H_2O$, where x' is the BET pore volume of the first stage calcined material in mℓ/g, and y' is the total mass of the first stage calcined material to be impregnated in kg, is used during this second impregnation, and is dissolved in sufficient distilled water such that the final volume of the solution is >x'y' litre; this solution is heated to a temperature between 60 and 95°C, to this solution is added the final inventory of y' kg of the first stage calcined material is added at atmospheric pressure, whilst continuous mixing of the slurry is maintained; with the gradual application of vacuum, under continuous mixing at a temperature between 60 and 95°C, the L.O.I. content of the slurry is reduced, over 3 or more hours, to the state of incipient wetness; at the stage of incipient wetness, a vacuum of <20kPa(a) is applied whilst simultaneously ensuring that the temperature does not drop below 60°C under continuous mixing; once the stage of incipient wetness has been reached, vacuum drying proceeds in an uninterrupted fashion, at the conditions: temperature >60°C, but not higher than 95°C, and a vacuum of <20kPa(a); vacuum drying under these specific conditions is maintained until a L.O.I. <90% of the L.O.I. value at incipient wetness has been reached; direct calcination of this dried material at 200°C to 300°C is then effected.

14. A method according to Claim 13 wherein, during either, or both, of the two slurry phase cobalt impregnation steps, a water soluble precursor salt of Pt or Pd is added, as a dopant capable of enhancing the reducibility of the active component, with the mass proportion of this dopant to cobalt being between 0,01:100 and 0,3:100.

15. A catalyst, when produced by the method of any one of Claims 10 to 14 inclusive.

16. A process for producing hydrocarbons, which includes contacting a synthesis gas comprising hydrogen (H_2) and carbon monoxide (CO) at an elevated temperature between

180°C and 250°C and an elevated pressure between 10 and 40 bar with a catalyst as claimed in Claim 15, after activation or reduction thereof, to obtain hydrocarbons, by means of a slurry phase Fischer-Tropsch reaction of the hydrogen with the carbon monoxide.

17. A novel method of treating a catalyst support, substantially as described and illustrated herein.

18. A novel protected modified catalyst support, substantially as described and illustrated herein.

19. A novel method of forming a catalyst, substantially as described and illustrated herein.

20. A novel activated or reduced catalyst, substantially as described and illustrated herein.

21. A novel process for producing hydrocarbons, substantially as described and illustrated herein.

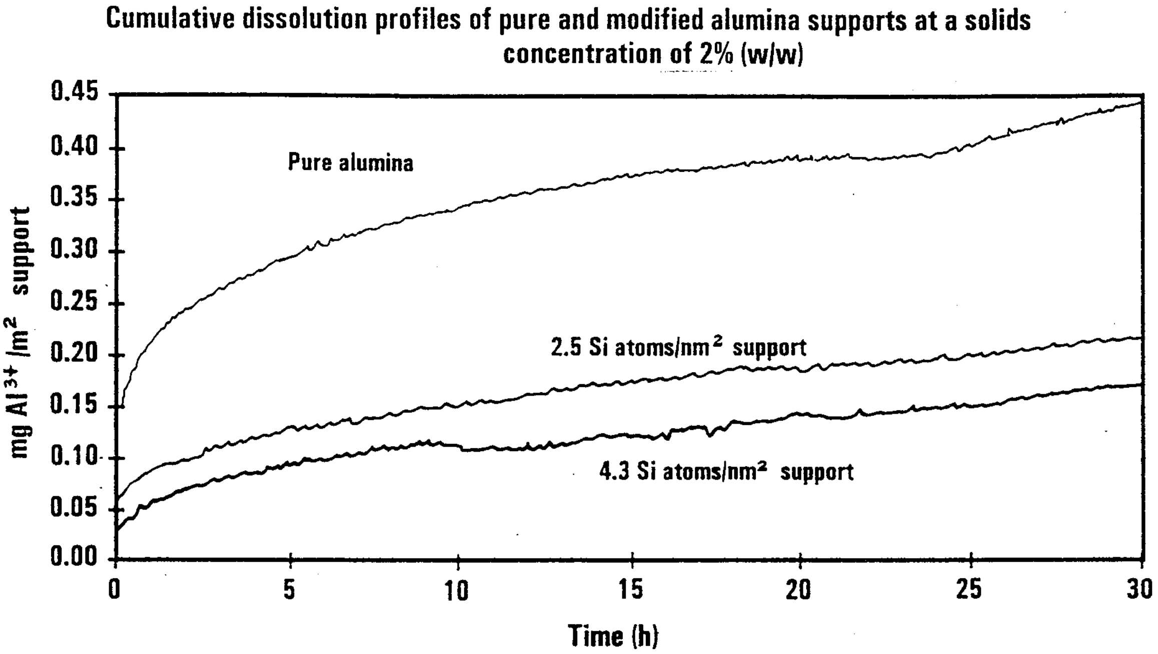

Cumulative dissolution profiles of pure and modified alumina supports at a solids concentration of 2% (w/w)
mg Al^{3+} /m^2 support
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
Pure alumina
2.5 Si atoms/nm^2 support
4.3 Si atoms/nm^2 support
0
5
10
15
20
25
30
Time (h)

FIG 1

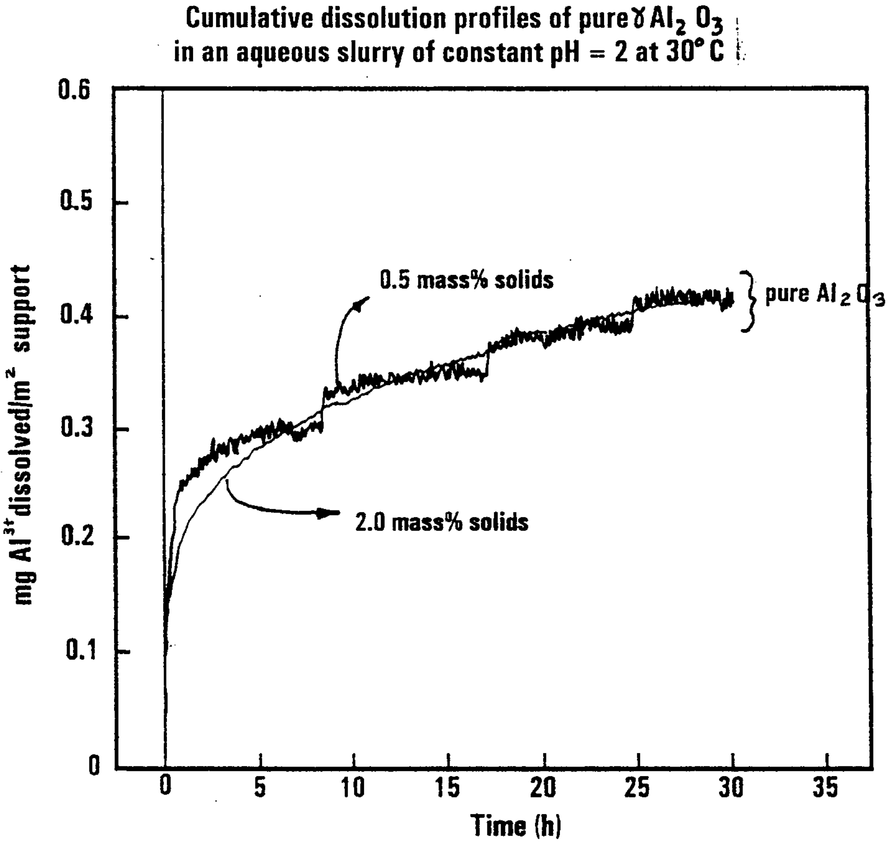

Cumulative dissolution profiles of pure γ Al$_2$ O$_3$ in an aqueous slurry of constant pH = 2 at 30° C
mg Al^{3+} dissolved/m^2 support
0.6
0.5
0.4
0.3
0.2
0.1
0
0.5 mass% solids
2.0 mass% solids
pure Al$_2$ O$_3$
0
5
10
15
20
25
30
35
Time (h)

FIG 2

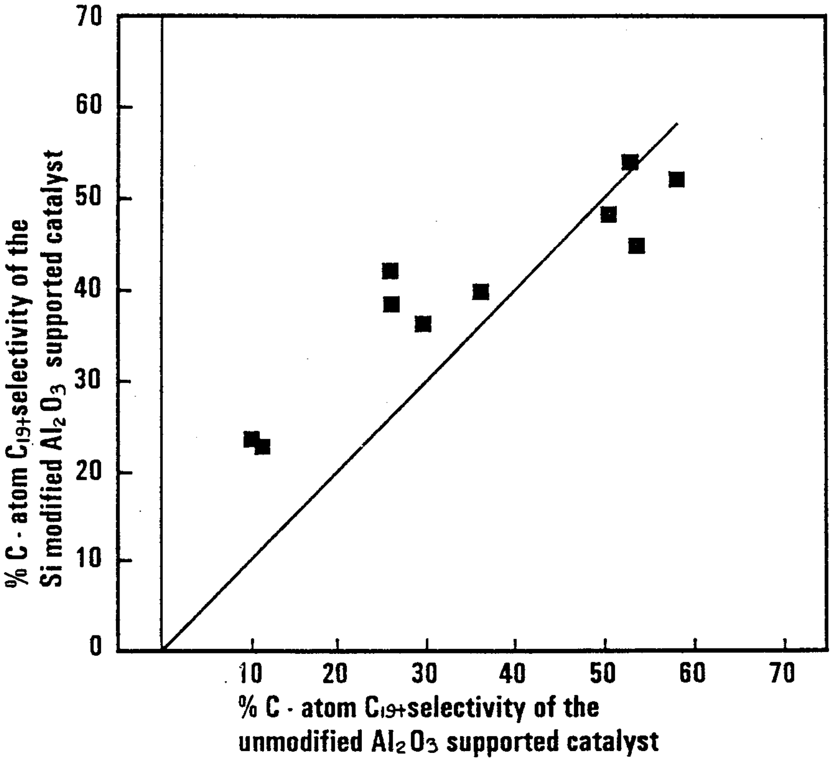

70
60
50
40
30
20
10
0
10
20
30
40
50
60
70
% C - atom C_{19}+selectivity of the Si modified Al_2O_3 supported catalyst
% C - atom C_{19}+selectivity of the unmodified Al_2O_3 supported catalyst

FIG 3

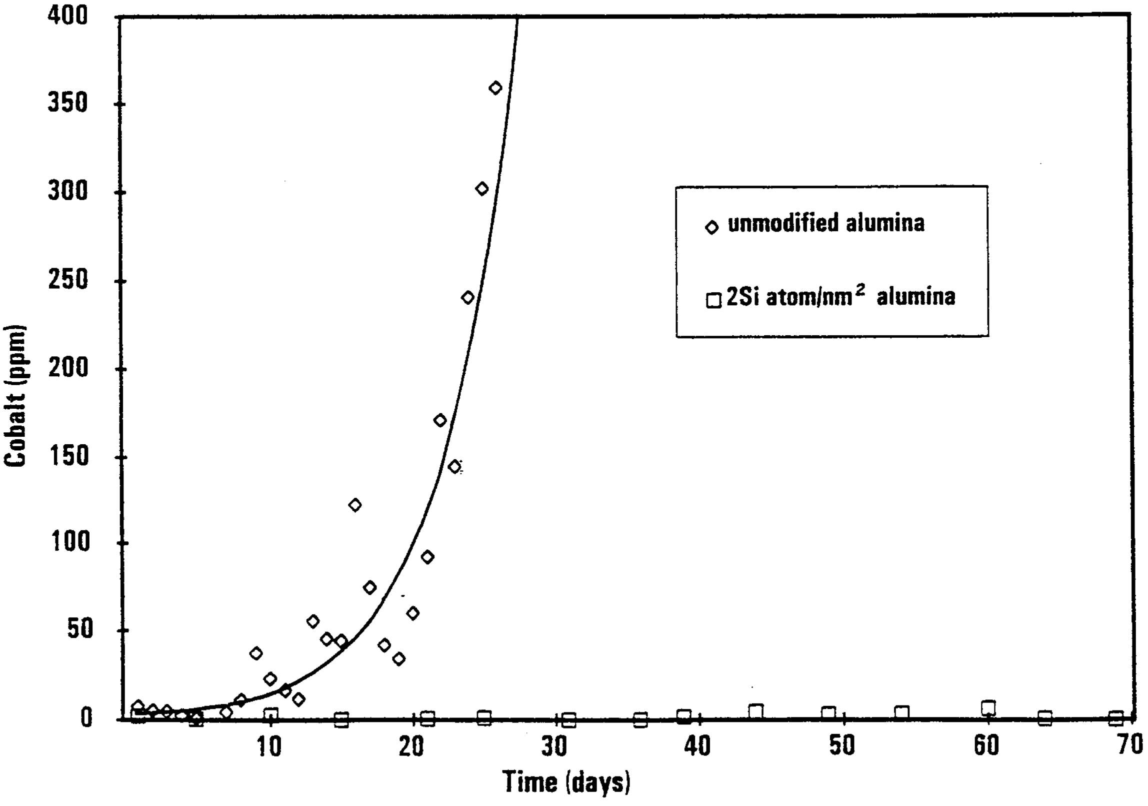

400
350
300
250
200
150
100
50
0
10
20
30
40
50
60
70
Cobalt (ppm)
Time (days)
◇ unmodified alumina
□ 2Si atom/nm^2 alumina

FIG 4

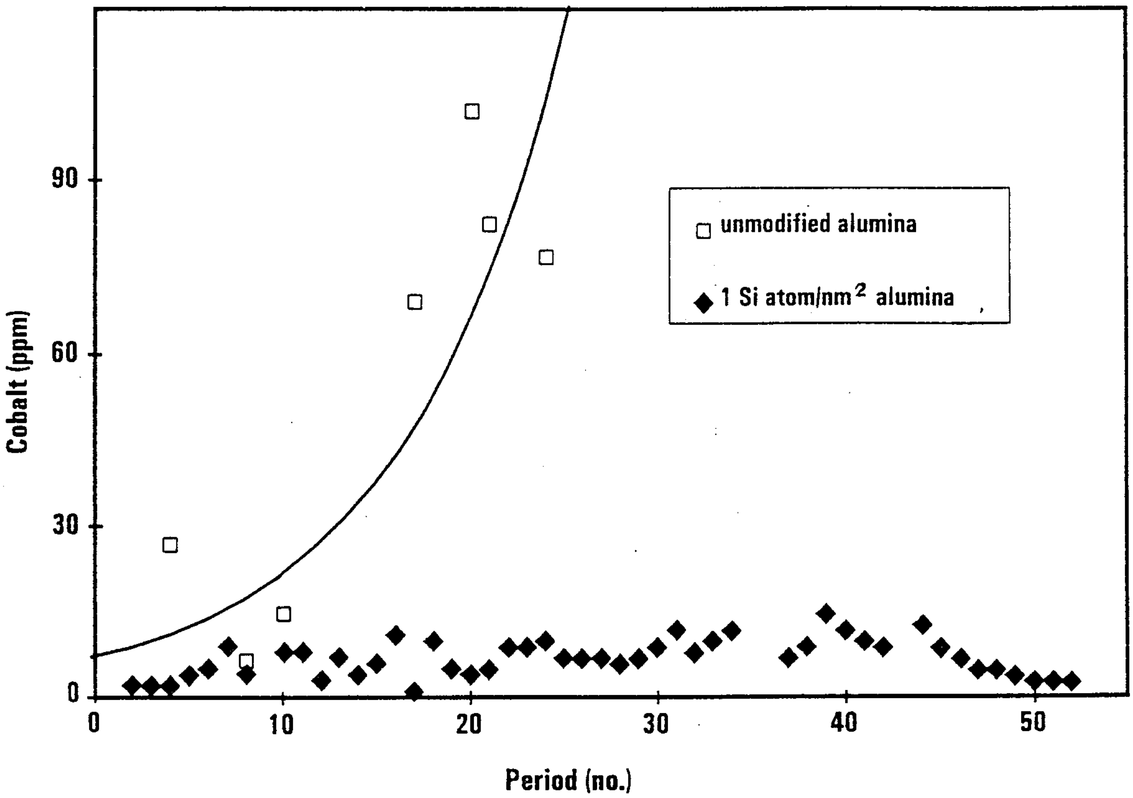


FIG 5

Cumulative dissolution profiles of pure and modified titania supports at a solids concentration of 2% (w/w)

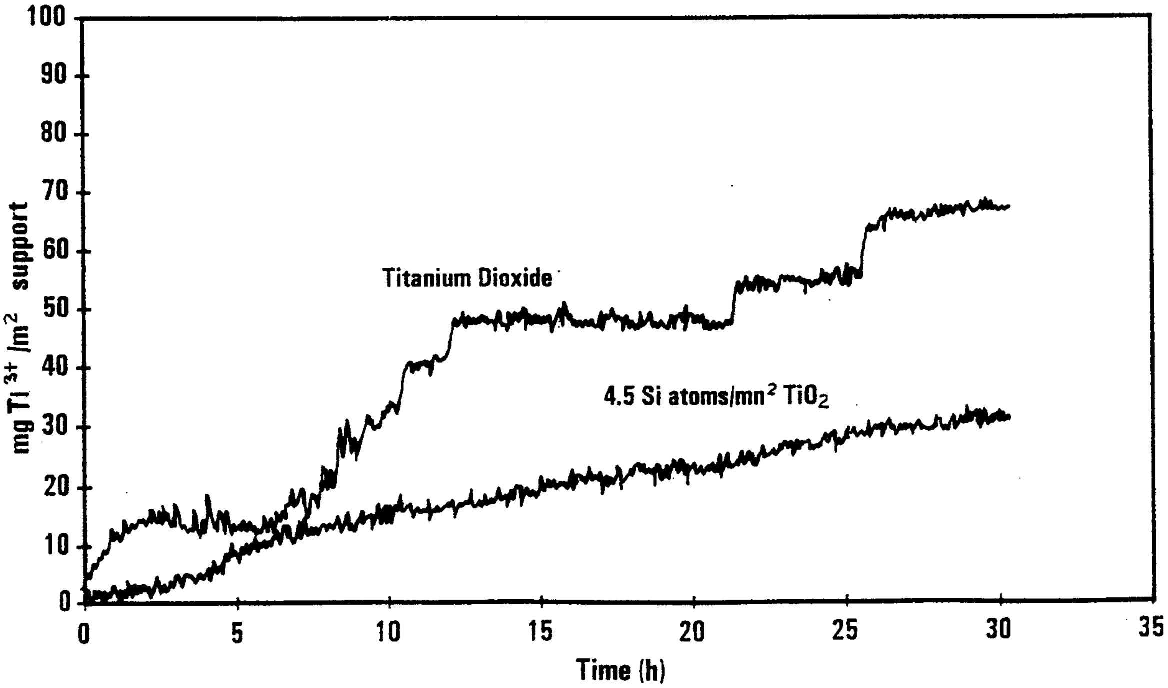


FIG 7

Cumulative dissolution profiles for unmodified and modified alumina supports at a solids concentration of 2% (w/w)

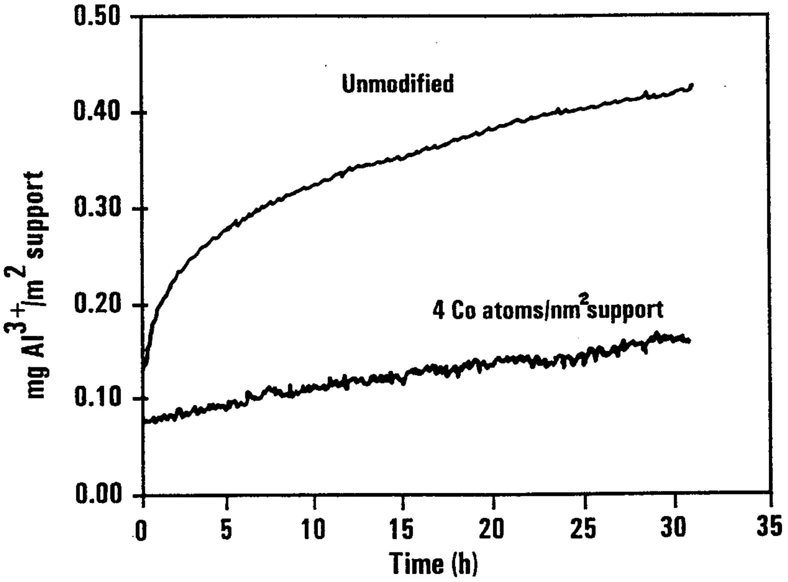


FIG 6

Cumulative dissolution profiles of pure and modified alumina supports at a solids concentration of 2% (w/w)

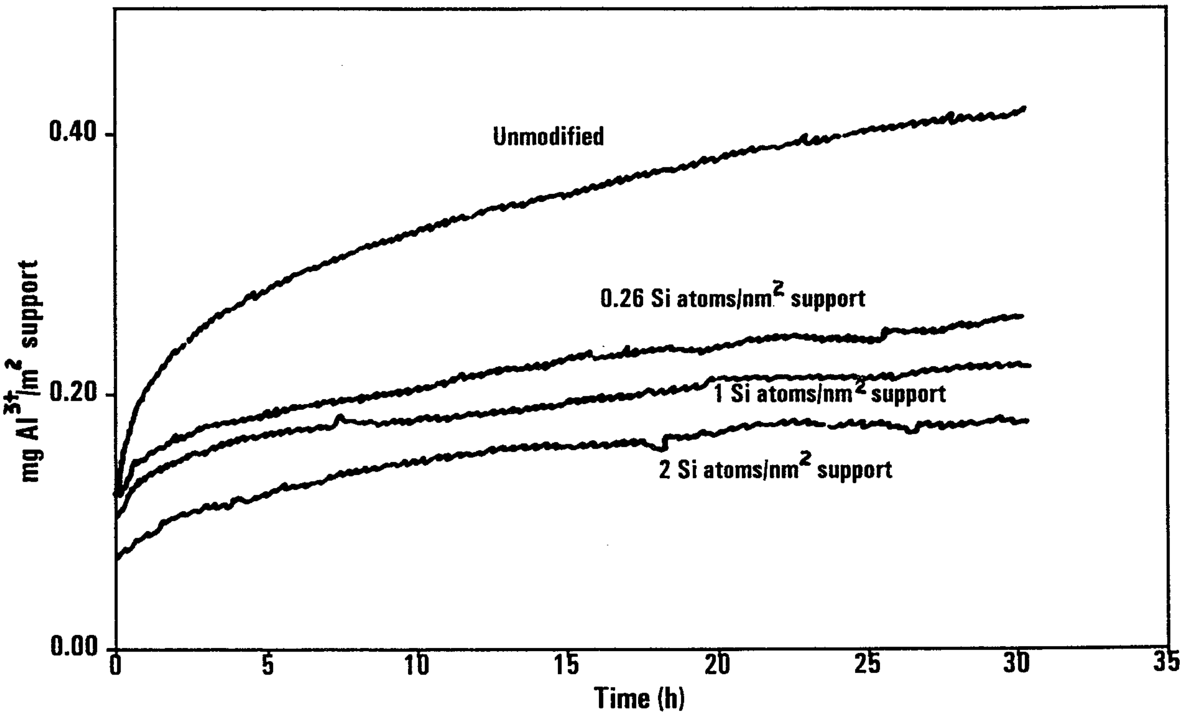


FIG 8

Cobalt content in secondary filtered wax for pure and modified supported catalysts

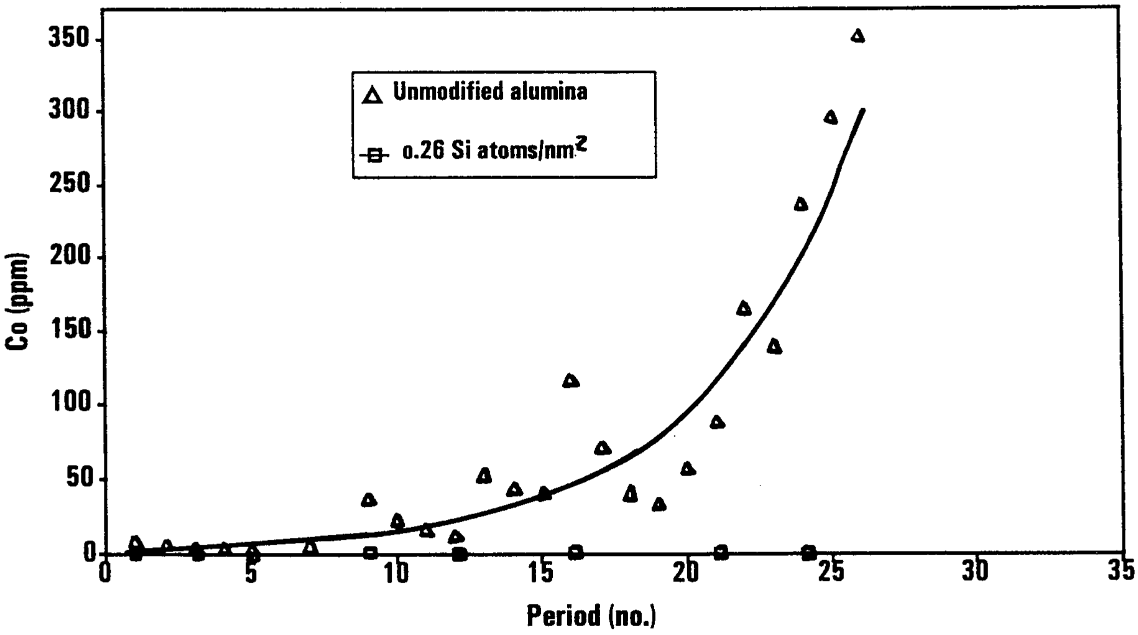
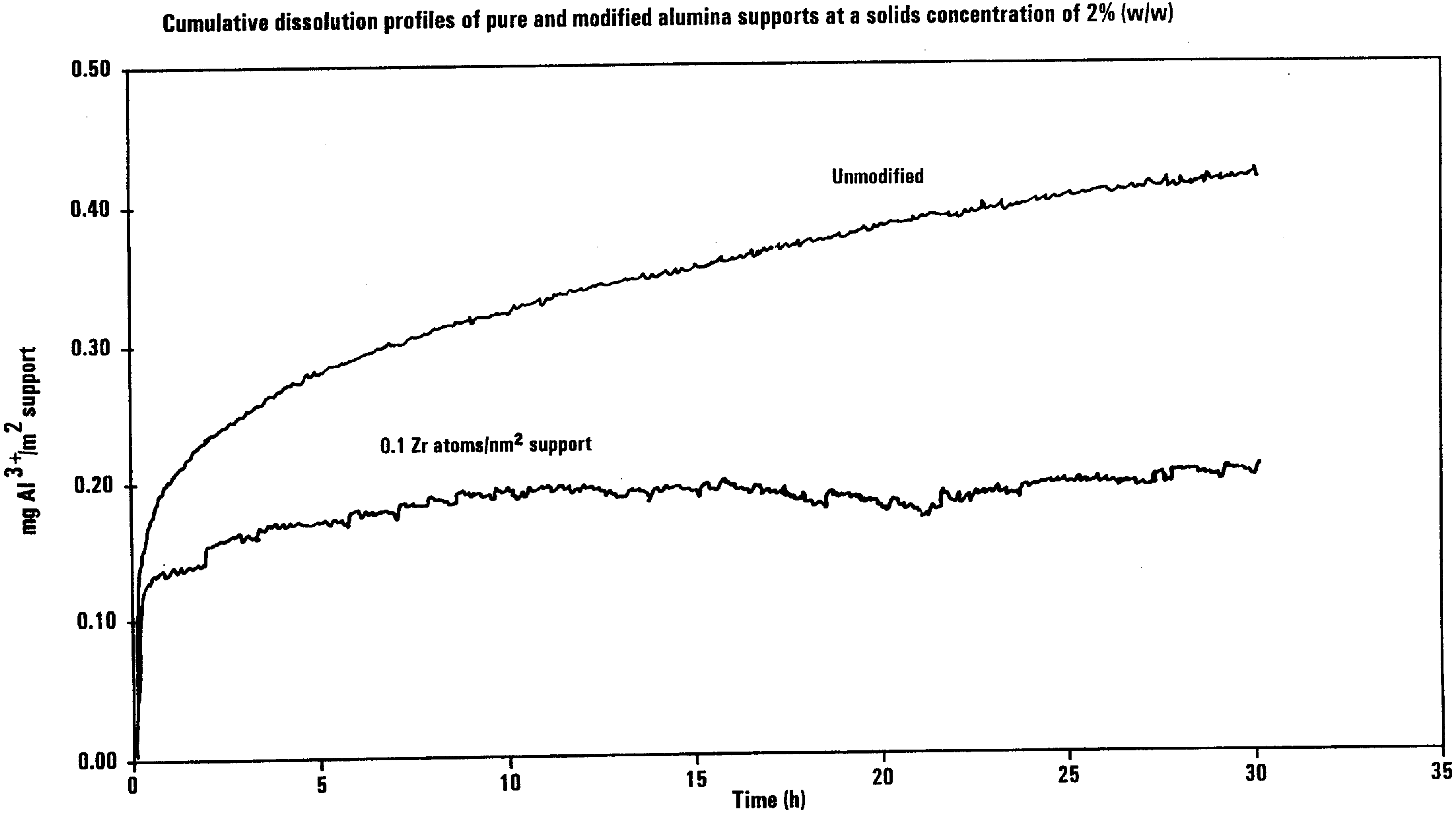


FIG 9



Cumulative dissolution profiles of pure and modified alumina supports at a solids concentration of 2% (w/w)

FIG 10

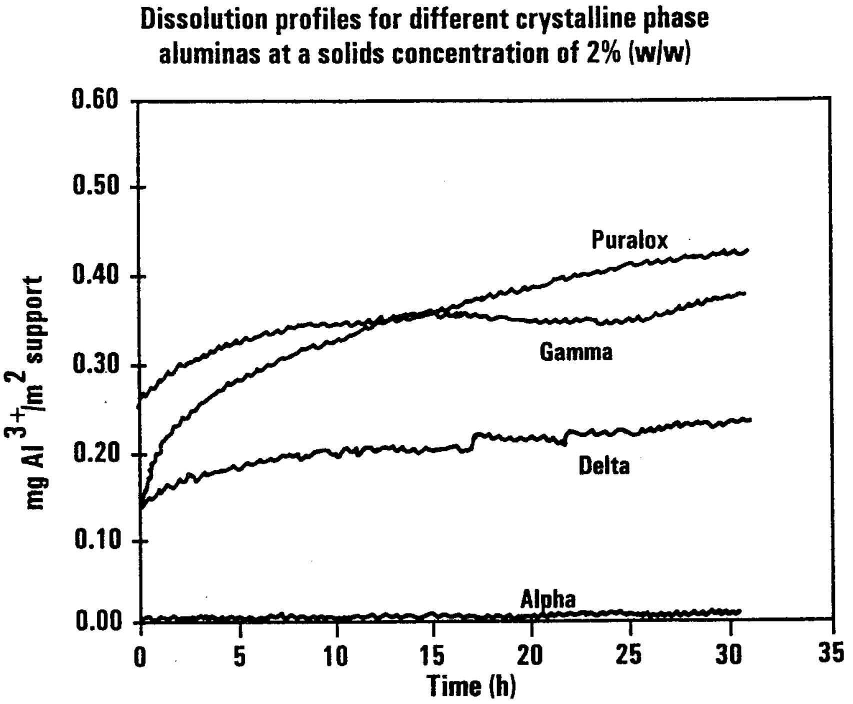

Dissolution profiles for different crystalline phase aluminas at a solids concentration of 2% (w/w)
mg Al $^{3+}$/m ^{2} support
0.60
0.50
0.40
0.30
0.20
0.10
0.00
0
5
10
15
20
25
30
35
Time (h)
Puralox
Gamma
Delta
Alpha

FIG 11

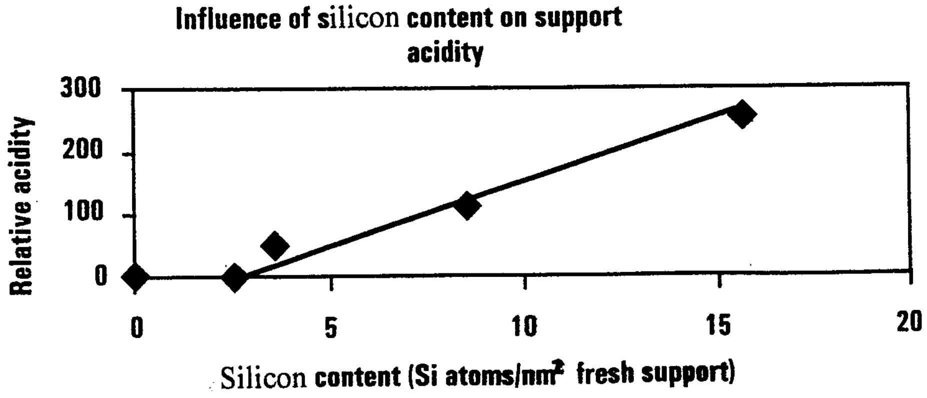

Influence of silicon content on support acidity
Relative acidity
300
200
100
0
0
5
10
15
20
Silicon content (Si atoms/nm^2 fresh support)

FIG 12

INTERNATIONAL SEARCH REPORT

Inter ɔnal Application No
PCT/GB 99/00527

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B01J33/00 B01J23/75 C07C1/04 B01J37/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B01J C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 141 596 A (ATOMIC ENERGY OF CANADA LTD) 15 May 1985	
A	EP 0 586 196 A (CROSFIELD JOSEPH & SONS) 9 March 1994	
A	WO 97 20216 A (GRACE W R & CO) 5 June 1997	
A	US 5 169 821 A (SOLED STUART L ET AL) 8 December 1992	

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search 4 June 1999	Date of mailing of the international search report 14/06/1999
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Thion, M

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INTERNATIONAL SEARCH REPORT

Inter nal Application No
PCT/GB 99/00527

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0141596 A	15-05-1985	CA 1200540 A	11-02-1986
		JP 60094142 A	27-05-1985
		US 4536488 A	20-08-1985
EP 0586196 A	09-03-1994	AU 4603393 A	10-03-1994
		BR 9303653 A	22-03-1994
		CA 2105000 A	02-03-1994
		JP 6205979 A	26-07-1994
WO 9720216 A	05-06-1997	AU 7484796 A	19-06-1997
US 5169821 A	08-12-1992	AU 650177 B	09-06-1994
		AU 2840692 A	20-05-1993
		CA 2080645 A	15-05-1993
		DE 69205663 D	30-11-1995
		DE 69205663 T	21-03-1996
		EP 0542527 A	19-05-1993
		NO 301153 B	22-09-1997
		US 5397806 A	14-03-1995