



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : C07C 2/56, 2/58, B01J 20/34 B01J 38/48, 38/50, 38/52	A1	(11) International Publication Number: WO 93/10065 (43) International Publication Date: 27 May 1993 (27.05.93)
(21) International Application Number: PCT/US92/10095 (22) International Filing Date: 23 November 1992 (23.11.92) (30) Priority data: 07/796,940 22 November 1991 (22.11.91) US (60) Parent Application or Grant (63) Related by Continuation US 07/796,940 (CIP) (71) Applicant (for all designated States except US): CATALYTICA, INC. [US/US]; 430 Ferguson Drive, Building 3, Mountain View, CA 94043 (US).		(72) Inventors; and (75) Inventors/Applicants (for US only) : COOPER, Michael, D. [US/US]; 1349 Yosemite Avenue, San Jose, CA 95126 (US). RAO, Pradip [US/US]; 6221 Balderstone Drive, San Jose, CA 95120 (US). KING, David, L. [US/US]; 713 Rustic Lane, Mountain View, CA 94049 (US). LOPEZ, Ronald, R. [US/US]; 2855 Berryessa Road, San Jose, CA 95132 (US). (74) Agents: WHEELLOCK, E., Thomas et al.; Morrison & Forster, 755 Page Mill Road, Palo Alto, CA 94304-1003 (US). (81) Designated States: AT, AU, BB, BG, BR, CA, CH, CS, DE, DK, ES, FI, GB, HU, JP, KP, KR, LK, LU, MG, MN, MW, NL, NO, PL, RO, RU, SD, SE, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: METHOD FOR REGENERATING CERTAIN ACIDIC HYDROCARBON CONVERSION CATALYSTS BY SOLVENT EXTRACTION (57) Abstract This invention is a process for the regeneration of solid acidic hydrocarbon conversion catalysts, but particularly certain transition aluminas and zeolites promoted with Lewis acids (preferably BF₃) which have been used in the alkylation of isoparaffins with olefins. The process involves the removal of some portion of the reaction product residue adhering to the solid catalyst by contact with a solvent to partially recover the catalyst's initial activity.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FR	France	MR	Mauritania
AU	Australia	GA	Gabon	MW	Malawi
BB	Barbados	GB	United Kingdom	NL	Netherlands
BE	Belgium	GN	Guinea	NO	Norway
BF	Burkina Faso	GR	Greece	NZ	New Zealand
BG	Bulgaria	HU	Hungary	PL	Poland
BJ	Benin	IE	Ireland	PT	Portugal
BR	Brazil	IT	Italy	RO	Romania
CA	Canada	JP	Japan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SK	Slovak Republic
CI	Côte d'Ivoire	LI	Liechtenstein	SN	Senegal
CM	Cameroon	LK	Sri Lanka	SU	Soviet Union
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	MC	Monaco	TG	Togo
DE	Germany	MG	Madagascar	UA	Ukraine
DK	Denmark	ML	Mali	US	United States of America
ES	Spain	MN	Mongolia	VN	Viet Nam
FI	Finland				

METHOD FOR REGENERATING CERTAIN ACIDIC HYDROCARBON
CONVERSION CATALYSTS BY SOLVENT EXTRACTION
(PA-0084)

5

RELATED APPLICATIONS

This is a continuation-in-part of U.S. Patent Application Nos.
07/588,448 to Cooper et al. entitled "ISOPARAFFIN ALKYLATION USING A
10 LEWIS ACID PROMOTED TRANSITION ALUMINA CATALYST (PA-0017)" filed
September 26, 1990; 07/697,318 to Cooper et al. entitled "ISOPARAFFIN
ALKYLATION USING A LEWIS ACID PROMOTED TRANSITION ALUMINA
CATALYST (PA-0060)" filed May 7, 1991; and 07/697,320 to Cooper et al.
entitled "LEWIS ACID PROMOTED TRANSITION ALUMINA CATALYSTS
15 SUITABLE FOR ISOPARAFFIN ALKYLATION (PA-0051)" filed May 7, 1991; the
entirety of which are incorporated by reference. This application is also
related to U.S. Patent Application No. 07/718,394 to Rao et al. entitled "A
METHOD FOR REGENERATING LEWIS ACID-PROMOTED TRANSITION
ALUMINA CATALYSTS USED FOR ISOPARAFFIN ALKYLATION BY
20 CALCINATION (PA-0061)" filed June 20, 1991; the entirety of which is
incorporated by reference.

FIELD OF THE INVENTION

This invention is a process for the regeneration of solid acidic
25 hydrocarbon conversion catalysts, but particularly certain transition aluminas
and zeolites promoted with Lewis acids (preferably BF_3) which have been
used in the alkylation of isoparaffin with olefins. The process involves the
removal of some portion of the reaction product residue adhering to the solid
catalyst by contact with a solvent to partially recover the catalyst's initial
30 activity.

BACKGROUND OF THE INVENTION

There are a wide variety of hydrocarbon conversion processes using
strongly acidic solid acid catalysts at temperatures low enough to maintain the

reaction medium in a liquid phase. These processes include oligomerization, alkylation, isomerization, hydroisomerization, etc. The catalysts for these processes include such disparate acidic materials as acidic zeolites, alumina, silica-alumina, silica, boron oxides, phosphorus oxides, titanium oxide, zirconium oxide, chromia, zinc oxide, magnesia, calcium oxide, silica-alumina-zirconia, chromia-alumina, alumina-boria, silica-zirconia, aluminum phosphate molecular sieves, silicoaluminophosphate molecular sieves, solid polymeric ion exchange resins, tetravalent metal phosphonates with pendent acid groups, sulfated metal oxides (such as alumina), and the like. These catalysts may be treated with or complexed with Lewis acids. A side reaction in many of these processes produces what appears to be a low level polymer or oligomer. Unlike many higher temperature processes, the side products are not coke-like in nature. These poorly characterized side reaction products, or "gunk", may be at least partially removed using solvent extraction procedures and carefully chosen solvents. One process, with its concomitant catalyst, to which solvent extraction is especially applicable is isoparaffin/olefin alkylation using solid acid catalysts particularly zeolites or aluminas which have been treated with Lewis acids.

The preparation of high octane blending components for motor fuels using strong acid alkylation processes (notably where the acid is hydrofluoric acid or sulfuric acid) is well-known. Alkylation is the reaction in which an alkyl group is added to an organic molecule (typically an aromatic or olefin). For production of gasoline blending stocks, the reaction is between an isoparaffin and an olefin. Alkylation processes have been in wide use since World War II when high octane gasolines were needed to satisfy demands from high compression ratio or supercharged aircraft engines. The early alkylation units were built in conjunction with fluid catalytic cracking units to take advantage of the light end by-products of the cracking units: isoparaffins and olefins. Fluidized catalytic cracking units still constitute the major source of feedstocks for gasoline alkylation units. In spite of the mature state of strong acid alkylation technology, existing problems with the hydrofluoric and sulfuric acid technologies continue to be severe: disposal of the used acid, unintentional

emission of the acids during use or storage, substantial corrosivity of the acid catalyst systems, and other environmental concerns.

Although a practical alkylation process using solid acid catalysts having little or no corrosive components has long been a goal, commercially viable processes do not exist.

The open literature shows several systems used to alkylate various hydrocarbon feedstocks.

The American Oil Company obtained a series of patents in the mid-1950's on alkylation processes involving C₂-C₁₂ (preferably C₂ or C₃) olefins and C₄-C₈ isoparaffins. The catalysts used were BF₃-treated solids and the catalyst system (as used in the alkylation process) also contained free BF₃. A summary of those patents is found in the following list:

	<u>Patent No.</u>	<u>Inventor</u>	<u>BF₃-Treated Catalyst* (with free BF₃)</u>
	2,804,491	Kelly <u>et al.</u>	SiO ₂ stabilized Al ₂ O ₃ (10%-60% by weight BF ₃)
20	2,824,146	Kelly <u>et al.</u>	metal pyrophosphate hydrate
	2,824,150	Knight <u>et al.</u>	metal sulfate hydrate
	2,824,151	Kelly <u>et al.</u>	metal stannate hydrate
	2,824,152	Knight <u>et al.</u>	metal silicate hydrate
	2,824,153	Kelly <u>et al.</u>	metal orthophosphate hydrate
25	2,824,154	Knight <u>et al.</u>	metal tripolyphosphate hydrate
	2,824,155	Knight <u>et al.</u>	metal pyroarsenate hydrate
	2,824,156	Kelly <u>et al.</u>	Co or Mg arsenate hydrate
	2,824,157	Knight <u>et al.</u>	Co, Al, or Ni borate hydrate
	2,824,158	Kelly <u>et al.</u>	metal pyroantimonate hydrate salt
30	2,824,159	Kelly <u>et al.</u>	Co or Fe molybdate hydrate
	2,824,160	Knight <u>et al.</u>	Al, Co, or Ni tungstate hydrate
	2,824,161	Knight <u>et al.</u>	borotungstic acid hydrate or Ni or Cd borotungstate hydrate
	2,824,162	Knight <u>et al.</u>	phosphomolybdic acid hydrate
35	2,945,907	Knight <u>et al.</u>	solid gel alumina (5%-100% by weight of Zn or Cu fluoborate, preferably anhydrous)

*may be supported on Al₂O₃

None of these disclose a process for regenerating an alkylation catalyst using

a solvent extraction process for ⁴regenerating the catalyst.

Acid catalysts used to oligomerize olefins are known. U.S. Patent No. 2,748,090 to Watkins suggests the use of a catalyst made up of a Group VIII metal (preferably nickel), a phosphoric acid (preferably containing phosphorus pentoxide), placed on an alumina adsorbent, and pretreated with BF_3 . Alkylation of aromatics is suggested.

U.S. Patent No. 2,976,338 to Thomas suggests a polymerization catalyst comprising a complex of BF_3 or H_3PO_4 optionally on an adsorbent (such as activated carbon) or a molecular sieve optionally containing potassium acid fluoride.

Certain references suggest the use of alumina-containing catalysts for alkylation of aromatic compounds. U.S. Patent No. 3,068,301 to Hervert *et al.* suggests a catalyst for alkylating aromatics using "olefin-acting compounds". The catalyst is a solid, silica-stabilized alumina up to 10% SiO_2 , all of which has been modified with up to 100% by of weight BF_3 .

Other BF_3 -treated aluminas are known. For instance, U.S. Patent No. 3,114,785 to Hervert *et al.* suggests the use of a BF_3 -modified, substantially anhydrous alumina to shift the double bond of 1-butene to produce 2-butene. The preferred alumina is substantially anhydrous gamma-alumina, eta-alumina, or theta-alumina. The various aluminas will adsorb or complex with up to about 19% by weight fluorine depending upon the type of alumina and the temperature of treatment.

In U.S. Patent No. 4,407,731 to Imai a high surface area metal oxide such as alumina (particularly gamma-alumina, eta-alumina, theta-alumina, silica, or a silica-alumina) is used as a base or support for BF_3 . The BF_3 treated metal oxide is used for generic oligomerization and alkylation reactions. The metal oxide is treated in a complicated fashion prior to being treated with BF_3 . The first step entails treating the metal oxide with an acid solution and with a basic aqueous solution. The support is washed with an aqueous decomposable salt such as ammonium nitrate. The support is washed using deionized H_2O until the wash water shows no alkali or alkaline earth metal cations in the filtrate. The support is dried and calcined. The

disclosure suggests generically that BF_3 is then introduced to the treated metal oxide support. The examples show introduction of the BF_3 at elevated temperatures, e.g, 300°C or 350°C.

Similarly, U.S. Patent No. 4,427,791 to Miale et al. suggests the enhancement of the acid catalytic activity of inorganic oxide materials (such as alumina or gallia) by contacting the material with ammonium fluoride or boron fluoride, contacting the treated inorganic oxide with an aqueous ammonium hydroxide or salt solution, and calcining the resulting material. The inorganic oxides treated in this way are said to exhibit enhanced Brønsted acidity and, therefore, is said to have improved acid activity towards the catalysis of numerous and several reactions (such as alkylation and isomerization of various hydrocarbon compounds). A specific suggested use for the treated inorganic oxide is as a matrix or support for various zeolite materials ultimately used in acid catalyzed organic compound conversion processes.

U.S. Patent No. 4,751,341 to Rodewald shows a process for treating a ZSM-5 type zeolite with BF_3 to reduce its pore size, enhance its shape selectivity, and increase its activity towards the reaction of oligomerizing olefins. The patent also suggests using these materials for alkylation of aromatic compounds.

Certain Soviet publications suggest the use of Al_2O_3 catalysts for alkylation processes. Benzene alkylation using those catalysts (with 3 ppm to 5 ppm water and periodic additions of BF_3) is shown in Yagubov, Kh. M. et al., Azerb. Khim. Zh., 1984, (5) p. 58. Similarly, Kozorezov, Yu and Levitskii, E.A., Zh. Print. Khim. (Leningrad), 1984, 57 (12), p. 2681, show the use of alumina which has been treated at relatively high temperatures and modified with BF_3 at 100°C. There are no indications that BF_3 is maintained in excess. Isobutane alkylation using $\text{Al}_2\text{O}_3/\text{BF}_3$ catalysts is suggested in Neftekhimiya, 1977, 17 (3), p. 396; 1979, 19 (3), P. 385. The olefin is ethylene. There is no indication that BF_3 is maintained in excess during the reaction. The crystalline form of the alumina is not described nor is any method suggested for regeneration of the catalysts.

U.S. Patent No. 4,918,255 to Chou et al. suggests a process for the

alkylation of isoparaffins and olefins using a composite described as "comprising a Lewis acid and a large pore zeolite and/or a non-zeolitic inorganic oxide". The process disclosed requires isomerization of the olefin feed to reduce substantially the content of alpha-olefin and further suggests that water addition to the alkylation process improves the operation of the process.

U.S. Patent No. 4,992,616 to Chou et al. deals with the process noted above for alkylation of isoparaffins and olefins using a composite described as "comprising a Lewis acid and a large pore zeolite" but requires addition of water for improving the operation of the process. The best Research Octane Number (RON) product shown in the examples and made using the disclosed invention is 86.0 (Table 2).

Similarly, PCT published applications WO 90/00533 and 90/00534 (which are based in part on the U.S. patent to Chou et al. noted above) suggest the same process as does Chou et al. WO 90/00534 is specific to a process using boron trifluoride-treated inorganic oxides including "alumina, silica, boria, oxides of phosphorus, titanium oxide, zirconium oxide, chromia, zinc oxide, magnesia, calcium oxide, silica-alumina-zirconia, chromia-alumina, alumina-boria, silica-zirconia, and the various naturally occurring inorganic oxides of various states of purity such as bauxite, clay and diatomaceous earth". Of special note is the statement that the "preferred inorganic oxides are amorphous silicon dioxide and aluminum oxide". The examples show the use of amorphous silica (and BF_3) to produce alkylates having an RON of no greater than 94. U.S. Pat. Number 4,935,577 to Huss, Jr. et al. teaches a process for the catalytic distillation of various hydrocarbons by e.g., alkylation or oligomerization, using a catalyst "consisting essentially of a Lewis acid promoted inorganic oxide." The inorganic oxide may be selected from the non-zeolitic materials discussed above with regard to the Chou et al. published PCT applications. Additionally, the inorganic oxide may be a large pore crystalline molecular sieve.

There are a variety of disclosed ways to regenerate catalysts used in alkylation processes or using Lewis acids. Typical of such processes are the

following.

U.S. Patent No. 3,647,916, to Caesar et al. shows a process for isoparaffin-olefin alkylation using crystalline zeolite catalysts at low isoparaffin to olefin ratios. The zeolite is first steamed to reduce the number of acid sites and so reduce the amount of olefin polymerization which occurs. The isoparaffin is added to the catalyst before the olefin is introduced to further limit the amount of polymerization. There is no discussion of the use of auxiliary Lewis acids in conjunction with the zeolites. Nevertheless, the catalysts are susceptible to deactivation due to the "accumulation in the pores thereof of olefin polymerization products". The regeneration is carried out by burning the surface residue "in an oxygen-containing atmosphere at an elevated temperature in the range of about 800 to 1400° F" followed by a step in which the catalyst is contacted with an aromatic or polar solvent.

U.S. Patent No. 3,833,679 to Gardner et al. shows a paraffin isomerization process using an HSbF_6 catalyst supported on a fluorided alumina. The catalyst was regenerated by introduction of an HF stream sufficient to convert to any SbF_5 to HSbF_6 . No mention is made of removal of any hydrocarbonaceous materials from the catalyst using this treatment.

U.S. Patent No. 3,893,942 to Yang also shows a process for isoparaffin-olefin alkylation using crystalline zeolite catalysts. A small amount of a hydrogenation catalyst (Group VIII metal) is included in the zeolite. Hydrogen gas is periodically introduced into the zeolite (apparently after the catalyst has been partially deactivated) and restores the activity of the catalyst. Yang indicates that the nature of the chemical reaction between the hydrocarbonaceous deposit and the hydrogen is not clear but hydrogen is consumed and the alkylation activity is restored. This procedure is said to avoid "refractory coke deposits" formed when using high temperature inert gas regeneration treatments. Oxidative treatments are then said to be necessary. A paraffinic wash is desirably first applied to the catalyst to assist in the following hydrogenation step.

U.S. Patent No. 3,855,343 to Huang et al. teaches an isoparaffin-olefin alkylation process in which the catalyst is a combination of a macroreticular

acid cation exchange resin and boron trifluoride. The boron trifluoride is present in an amount in excess of that needed to saturate the resin. This catalyst is said to "age" and after some period of time must be regenerated. The catalyst is regenerated by solvent extraction with a polar solvent, preferably a low molecular weight alcohol.

The process disclosed in U.S. Patent No. 4,058,575 to Cahn *et al.* is a method of converting hydrocarbons, e.g., by alkylating them, in the presence of a Lewis acid and a strong Brønsted acid. Partially deactivated catalytic materials are pretreated with a hydrocarbon to remove contaminants and deactivated catalyst species.

The U.S. Patent No. 4,308,414 to Madgavkar shows a process for oligomerizing longer alpha-olefins using a particulate adsorbent (preferably SiO_2) and adsorbed boron trifluoride and water. The catalyst is regenerated by the procedure of adding a small amount of water with the feed olefin.

The U.S. Patent Nos. 4,914,256 and 4,992,614 to Rodewald suggest the reactivation of catalysts (particularly supported boron trifluoride-containing alkylation catalysts) used in a variety of hydrocarbon conversion catalysts by application of ultrasonic energy to the partially deactivated catalyst. The process is said to eliminate the need for separation of the catalyst from the feedstock nor to subject the catalyst to a "burn-off" operation.

One disclosure showing the use of SO_2 to regenerate catalysts is Seapan *et al.*, "Decoking and Regeneration of a Hydrotreating Catalyst by Supercritical Extraction", ACS Symposium Series 411, American Chemical Society, Washington, D.C., 1989. This disclosure shows the use of SO_2 (and other solvents) at pressures above their critical pressures to remove coke-type carbon species from hydrotreating catalysts. The use of SO_2 above 1200 psig is shown. The disclosure does not suggest the treatment of any catalysts which have non-coke residue.

These disclosures do not show the use of our liquid solvent extraction process to revive acidic catalysts having non-coke residue and especially those which are promoted with a Lewis acid (preferably BF_3) and which have been used in the alkylation of isoparaffin with olefins.

SUMMARY OF THE INVENTION

This invention is a solvent extraction process for the regeneration of solid acidic hydrocarbon conversion catalysts but particularly those acidic catalysts such as aluminas or zeolites which have been promoted with Lewis acids (preferably BF_3) and used in the alkylation of isoparaffins with olefins. The process involves contacting the solid acidic catalyst with a liquid solution comprising a solvent selected from SO_2 ; oxygenates such as C_1 - C_4 alcohols, ketones, and aldehydes; nitriles such as acetonitrile; and phenolics such as anisole and phenol. When the solid acidic catalyst additionally comprises a Lewis acid the process involves contacting the combination catalyst with a liquid solution comprising a solvent selected from SO_2 or from aromatic ethers and phenolics such as anisole and phenol.

The catalysts for these processes include such disparate acidic materials as acidic zeolites, alumina, silica-alumina, silica, boron oxides, phosphorus oxides, titanium oxide, zirconium oxide, chromia, zinc oxide, magnesia, calcium oxide, silica-alumina-zirconia, chromia-alumina, alumina-boria, silica-zirconia, aluminum phosphate molecular sieves, silicoaluminophosphate molecular sieves, solid polymeric ion exchange resins, tetravalent metal phosphonates with pendent acid groups, sulfated metal oxides (such as alumina), and the like. These catalysts may be treated with or complexed with Lewis acids. They are all acidic in their functionality as hydrocarbon conversion catalysts.

The alkylation process in which certain of the candidate catalysts are used produces alkylates suitable for use as very high octane, non-aromatic blending components in motor fuels. The alkylates are produced from olefins and isoparaffins. The catalyst used comprises one or more transitional aluminas which are treated with at least one Lewis acid, preferably BF_3 . The process optimally utilizes an amount of free Lewis acid and produces high octane alkylate.

The regeneration process includes the steps of separating the solid component from the liquid reaction medium (but preferably maintaining it in the substantial absence of oxygen and water) and contacting the solid with an

excess of the liquid solvent. The catalyst may be heated at a lower temperature prior to the solvent contact step so to volatilize certain hydrocarbons and to recover any complexed Lewis acid or may be washed with an inert solvent such as isobutane or other branched alkane.

5

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a graph of the results of the regeneration procedure of the invention as practiced in Example 1 upon an alumina-based alkylation catalyst over several liquid SO₂ regeneration cycles.

10

Figure 2 is an ¹¹B NMR graph of the catalyst used in Example 1 following several regeneration cycles.

DESCRIPTION OF THE INVENTION

This invention is a solvent extraction process for the regeneration of solid acidic hydrocarbon conversion catalysts but particularly those acidic catalysts such as aluminas or zeolites which have been promoted with Lewis acids (preferably BF₃) and used in the alkylation of isoparaffins with olefins. The process involves contacting the solid acidic catalyst (which does not contain a significant Lewis acid component) with a liquid solution comprising a solvent selected from SO₂; oxygenates such as C₁-C₄ alcohols, ketones, and aldehydes; nitriles such as acetonitrile; and phenolics such as anisole and phenol. When the solid acidic catalyst additionally comprises a Lewis acid, the process involves contacting the combination catalyst with a liquid solution comprising a solvent selected from SO₂ or from aromatic ethers and phenolics such as anisole and phenol.

25

The solid acid catalysts suitable for regeneration using these processes include such disparate acidic materials as acidic zeolites, alumina, silica-alumina, silica, boron oxides, phosphorus oxides, titanium oxide, zirconium oxide, chromia, zinc oxide, magnesia, calcium oxide, silica-alumina-zirconia, chromia-alumina, alumina-boria, silica-zirconia, aluminum phosphate molecular sieves, silicoaluminophosphate molecular sieves, solid polymeric ion exchange resins, tetravalent metal phosphates with pendent acid groups, sulfated metal

30

oxides (such as alumina), and the like. In particular, the zeolites are preferably large pore zeolitic materials such as zeolite L, zeolite X, zeolite Y, ZSM-4, ZSM-5, ZSM-11, ZSM-12, zeolite β , zeolite Ω , mordenite, and faujasite. The zeolites must be acidic but may be natural, synthetic, or may have framework substitutions of other metals. These catalysts may be treated with or complexed with Lewis acids. They are all acidic in their functionality as hydrocarbon conversion catalysts.

The preferred catalyst system for this regeneration process comprises certain transition aluminas which have been treated with one or more Lewis acids in combination with a minor amount of free Lewis acid. The alumina catalyst component is made by contacting free Lewis acid with certain transition alumina substrates.

The Alumina Catalyst Component

The preferred alumina catalyst component comprises or consists essentially of a major amount of transition aluminas (preferably eta- or gamma-alumina) which has been treated with a Lewis acid, preferably BF_3 . The catalyst component is acidic in nature and contains substantially no metals (except, of course, aluminum and the semi-metal boron) in catalytic amounts except as may be present in trace amounts in the BF_3 or alumina.

Alumina

Aluminum oxide (alumina) occurs abundantly in nature, usually in the form of a hydroxide in the mineral bauxite, along with other oxidic impurities such as TiO_2 , Fe_2O_3 , and SiO_2 . The Bayer process is used to produce a reasonably pure Al_2O_3 having a minor amount of Na_2O . The Bayer process Al_2O_3 is further treated to produce a variety of alumina hydroxides:

12

	<u>Material</u>	<u>Common Name</u>	<u>% H₂O</u>	<u>H₂O/ Al₂O₃</u>	<u>CAS Index No.</u>
	α -trihydrate	hygrargillite/gibbsite	35	3.0	14762-493
5	β -trihydrate	bayerite	35	3.0	20257-20-9 or 12252-72-1
	β -trihydrate	nordstrandite	35	3.0	13840-05-6
	α -monohydrate	boehmite	15	1.0	1318-23-6
	hydrate	psuedoboehmite	26	2.0	_____

10

The aluminum hydroxides may then be treated by heating to produce various activated or transition aluminas. For instance, the aluminum hydroxide known as boehmite may be heated to form a sequence of transition phase aluminas: gamma, delta, theta, and finally, alpha (see Wefers *et al.*, "Oxides and Hydroxides of Alumina", Technical Paper No. 19, Aluminum Company of America, Pittsburgh, PA, 1972, pp.1-51).

15

Transition aluminas (and their crystalline forms) include:

	gamma	tetragonal
20	delta	orthorhombic/tetragonal
	eta	cubic
	theta	monoclinic
	chi	cubic/hexagonal
	kappa	hexagonal
25	lambda	orthorhombic

Activated aluminas and aluminum hydroxides are used in various chemical processes as catalyst and adsorbents. The aluminas suitable for use in this process include the noted transition aluminas: gamma, delta, eta, theta, chi, kappa, or lambda. Especially preferred are gamma- and eta-aluminas. Mixtures of the two are also desirable.

30

Since it is difficult to produce a substantially pure single phase transition alumina, mixtures of various aluminas are tolerable. For instance, in the production of eta-alumina, gamma-alumina is often concurrently present in the resulting product. Indeed, x-ray diffraction analysis can only detect the

35

difference between the two phases with some difficulty. Aluminum hydroxides (boehmite, gibbsite, etc.) may be present in the predominately transition phase product in more than trivial amounts so long as they do not substantially affect the desired alkylation reaction.

5 The catalyst may be found in any appropriate form such as pellet, granules, bead, sphere, powder, or other shape to facilitate its use in fixed beds, moving beds, or fluidized beds.

Lewis Acids

10 If the catalyst system of the regeneration process uses one or more Lewis acids in conjunction with the acidic catalyst noted above, then the Lewis acids may one of those described below.

A Lewis acid is a molecule which can form another molecule or an ion by forming a complex in which it accepts two electrons from a second molecule or ion. Typical strong Lewis acids include boron halides such as
15 BF_3 , BCl_3 , BBr_3 , and BI_3 ; antimony pentachloride (SbF_5); aluminum halides (AlCl_3 and AlBr_3); titanium halides such as TiBr_4 , TiCl_4 , and TiCl_3 ; zirconium tetrachloride (ZrCl_4); phosphorus pentafluoride (PF_5); iron halides such as FeCl_3 and FeBr_3 ; and the like. Weaker Lewis acids such as tin, indium, bismuth,
20 zinc, or mercury halides are also acceptable.

Catalyst Preparation

The preferred alumina catalyst system may be prepared in situ in an alkylation reactor by passing the Lewis acid in gaseous form through the
25 vessel containing the transition alumina. Alternatively, the alumina may be contacted with the Lewis acid and later introduced into the reactor. In any case, the alumina should be substantially dry prior to contact with the Lewis acid and maintained in that state. Contact temperatures between -25°C and about 100°C are acceptable; a temperature between -25°C and 30°C is
30 preferred. The partial pressure of gaseous Lewis acid added to the alumina is not particularly important so long as a sufficient amount of Lewis acid is added to the alumina. We have found that treatment of the alumina with BF_3

at the noted temperatures will result in an alumina-BF₃¹⁴ complex containing BF₃ sufficient to carry out the alkylation. The alumina contains between 0.5% and 30% by weight of BF₃.

Obviously, the alumina or other catalyst may be incorporated into a binder prior to its treatment with Lewis acid. The binders may be clays (such as montmorillonite and kaolin) or silica based materials (such as gels or other gelatinous precipitates). Other binder materials include carbon and metal oxides such as alumina, silica, titania, zirconia, and mixtures of those metal oxides. The composition of the binders is not particularly critical but care must be taken that they not substantially interfere with the operation of the alkylation reaction.

Alkylation Process

The alkylation process used in one aspect of the invention involves contacting an isoparaffin with an olefin in the presence of the alumina-based catalyst discussed above and in the presence of some excess free Lewis acid.

Specifically, the catalyst of this invention is active at low temperatures (as low as -30°C) as well as at higher temperatures (nearing 50°C). Lower temperatures (-5°C to 15°C) are preferred because of the enhanced octane of the alkylate produced and are particularly preferred if the feedstream contains more than about 1% isobutylene. Higher temperatures also tend to produce larger amounts of polymeric materials. The pressure used in the alkylation process is not particularly critical. In general, the pressure must be kept high enough to maintain the reactants and products in the liquid phase, although the catalyst will produce alkylation products when the feedstock is gaseous. As a practical guideline, the process may be operated at atmospheric pressure to about 750 psig. The amount of catalyst used in the alkylation process depends upon a wide variety of disparate variables. Nevertheless, we have found that the Weight Hourly Space Velocity ("WHSV" = weight of olefin feed/hour ÷ weight of catalyst) may effectively be between 0.1 and 120, especially between 0.5 and 30. The overall molar ratio of

isoparaffin to olefin is between about 1.0 and 50.0. Preferred ranges include 2.0 and 25.0; the more preferred include 3.0 and 12.0.

5 The feedstreams introduced into the catalyst desirably comprise isoparaffins having from four to ten carbon atoms and, most preferably, four to six carbon atoms. Isobutane is most preferred because of its ability to make high octane alkylate. The olefins desirably contain from three to five carbon atoms, i.e., propylene, cis- and trans-butene-2, butene-1, and

amylene.

10 The products of this alkylation process typically contain a complex mixture of highly branched alkanes. For instance, when using isobutane as the alkane and n-butylene as the olefin, a mixture of 2,2,3-; 2,2,4-; 2,3,3-; and 2,3,4-trimethylpentane (TMP) will result often with minor amounts of other isomeric or polymeric products.

15 The process involved may utilize the catalyst in a fixed bed using single or multiple feeds. That is to say, the feedstocks may be independently introduced at one or more points throughout the bed or between multiple beds. Desirably, the catalyst is contacted with the feedstocks in one or more of continuously stirred reactors, preferably with feed to each reactor.

Regeneration Step

20 As we have discussed above, the regeneration step involves the steps of separating the solid catalytic material from the product of the hydrocarbon conversion process by use of a liquid-solid separation technique and followed by the step of contacting the catalytic material with a solvent capable of regenerating the material. The solvent desirably is selected from SO₂;

25 oxygenates such as C₁-C₄ alcohols, ketones, and aldehydes; alkylnitriles such as acetonitrile; and phenolics and aromatic ethers such as anisole and phenol. Most preferably, the solvent comprises SO₂.

30 The catalyst may be first contacted with an inert gas to strip any excess gaseous Lewis acid and light hydrocarbons from the solid catalyst component. The catalyst may also be treated using a mild heating step (e.g., 50° to 75°C) prior to the solvent contact step to further strip hydrocarbons from the solid. Additionally, the removal of hydrocarbons and excess Lewis

acid may be facilitated by contact with an inert gas such as helium, nitrogen, etc. The hydrocarbons and Lewis acid may be recycled as appropriate.

The process involves contacting the solid acidic catalyst with a liquid solution comprising a solvent selected from SO_2 ; oxygenates such as $\text{C}_1\text{-C}_4$ alcohols, ketones, and aldehydes; nitriles such as acetonitrile; and phenolics such as anisole and phenol. When the solid acidic catalyst additionally comprises a Lewis acid the process involves contacting the combination catalyst with a liquid solution comprising a solvent selected from SO_2 or from aromatic ethers and phenolics such as anisole and phenol.

Specifically, the regeneration step involves the contacting of the solid catalyst component with the liquid solvent stream. Clearly, the choice made for the step of physically contacting the catalyst is dependent in large part upon the specifics of the catalyst component itself. For instance, if the catalyst is in the form of tablets or extrudates or Pall rings (or the like) and are found in a fixed bed, the most appropriate way to contact the catalyst would be to pass the liquid solvent over the catalyst in the catalyst's fixed bed. If, the catalyst is used as a slurry, the catalyst may be transported to a vessel suitable for contacting the alumina component with a liquid stream and then separating the solid from the liquid. The reactor in such a process would likely be a good choice for such a vessel. We have found it to be desirable that the catalyst be kept out of contact with water and with oxygen.

The amount of solvent used should be sufficient to remove at least a portion of the reaction residue found on the catalyst component. The residue is ill-defined but often appears to be a moderately long-chained or polymeric material largely alkane in nature but with a minor olefinic character. The residues also often contain polyolefins and aromatic components in small concentrations. We do not consider this regeneration process to be appropriate for residue caused as a result of high temperature hydrocarbon conversion processes, at least those which produce graphitic or carbonaceous residues on the catalyst. Such residues typically have H/C ratios less than one. Although the amount is not believed to be critical, we have found that for most alumina-based alkylation catalysts, an amount of

about 100 gm. of solvent per gm. of catalyst is sufficient to regenerate the catalyst to at least 40 % of the prior activity.

The temperature of the contact step is also not critical but for alkylation catalysts, treatment in the range of 0°C to 50°C is appropriate.

5 When a solvent comprising SO₂ is utilized in the contact step to regenerate catalysts containing Lewis acids, the solvent should be generally dry; preferably it is substantially free of organic and inorganic bases and SO₃ and H₂SO₄. The level of these contaminants may be such that they do not
10 substantially affect the level of catalyst activity upon return to the hydrocarbon conversion medium. Hydrocarbonaceous diluents, such as are the products of the accompanying hydrocarbon conversion process often make suitable diluents for the solvent used to regenerate the catalyst.

 Once the steps outlined above are completed, the solid catalyst component may be again be treated with one or more Lewis acids as
15 specified above and returned to the hydrocarbon conversion step. It may be desirable when using SO₂ as the solvent and a gaseous Lewis acid to overpressure the gaseous Lewis acid (e.g., at a pressure above the pressure at which the reaction and/or the solvent treatment step is carried out) before returning the catalyst to service; although we do not wish to be bound by this
20 theory, we believe that the overpressure aids in sweeping or displacing the solvent from the catalyst surface.

 The invention has been disclosed by direct description. Below may be
25 found examples showing various aspects of the invention. The examples are only examples of the invention and are not to be used to limit the scope of the invention in any way.

EXAMPLES

30 Example 1

 This example shows the regeneration of an alumina-based catalyst which had been treated with BF₃ and then used with excess BF₃ in an

alkylation reaction. The feedstream to the alkylation step was a synthetically prepared feed simulating the hydroisomerized C₄ effluent from an MTBE unit (MTBE effluent).

5 The olefinic feedstock was prepared containing (by weight) 94% trans- and cis-2-butene, 5% butene-1, and 1% isobutylene. The feedstock was prepared by mixing the olefinic feedstock with isobutane such that the final molar ratio of isobutane to olefin was 6/1. This was fed to the alkylation reactor at a weight hourly space velocity (WHSV -- based on olefin) was 10.7. The reaction temperature was held to 0°C. Samples were periodically removed from the reactor for analysis by gas-liquid chromatography.

10 During each reaction step, the alkylation reaction was run until approximately 85 gm of olefin per gram of catalyst (i.e., the catalyst "age") had been processed. At that point, there was some indication of a loss of activity of the catalyst as evidenced by a decreasing amount of product C₈ content and a concomitant increase in the product C₁₂⁺ content. Additionally, a decrease in the (R+M)/2 as calculated from the gas-liquid chromatography data using well-known correlations (Hutson and Logan, "Estimate Alky Yield and Quality", Hydrocarbon Processing, September, 1975, pp. 107-108) was noted at about that catalyst age.

20 The catalyst was then regenerated using the following procedure:

1. 50 cc of isobutane were added to the alkylation reactor primarily to raise the liquid level to assist in washing back into solution any catalyst that had accumulated at the top of the reactor,
- 25 2. the liquid product and isobutane were removed from the reactor through a filtering frit using pressurized inert gas,
3. the reactor containing the spent catalyst was purged with inert gas at 15 cc/min for thirty minutes until the catalyst had the consistency of a free-flowing powder,
- 30 4. 150 ml. SO₂ were added to the reactor and the contents stirred

for 20 minutes,

- 5
5. SO₂ was withdrawn from the reactor using pressurized inert gas and recovered in a collection vessel. The flow of inert gas was continued until no liquid was present in the reactor,
6. steps 4 and 5 were repeated twice,
- 10
7. the system was flushed with flowing inert gas for 15 minutes at 15 cc/min.,
- 15
8. BF₃ was added to the reactor vessel containing the regenerated catalyst and pressurized to a total pressure of 60 psig of BF₃. This pressure was held for 15 minutes. The reactor was then depressurized and purged with inert gas for five minutes, and
- 20
9. step 8 was repeated with the exception that following the depressurization of the BF₃, the inert gas was allowed to purge the system for 20 minutes. The system was then ready for the next alkylation cycle.

Following regeneration, the same procedure to initiate the alkylation reaction was followed as with a fresh catalyst, with the exception that isobutane was added to the reactor containing the catalyst and stirred for approximately 30 minutes prior to addition of the BF₃. This was to insure that the catalyst was well mixed into the liquid medium.

The described procedures of alkylation followed by regeneration were repeated for a total of nine cycles.

30

The results of the product analysis from each cycle are summarized in Table 1 and Figure 1, indicating initial and final performance as measured by gas chromatographic analysis of the hydrocarbon effluent. The data clearly show that the full activity of the catalyst is restored using the regeneration

procedure.

Following the final alkylation cycle, the catalyst was again regenerated with SO₂ using the noted procedure. Analysis of the recovered catalyst by elemental analysis gave the following results:

5

Carbon, wt%	0.3
Boron, wt%	1.9
Fluorine, wt%	11.1
Sulfur, wt%	(below detection limits)

10

The low carbon and sulfur content of the catalyst show that the SO₂ regeneration procedure is very efficient. The SO₂ does not accumulate on the surface of the catalyst after regeneration. The boron and fluorine contents of the catalyst are very similar to that found on a fresh catalyst. Analysis of the boron-containing species by solid state NMR of boron (Fig. 2) shows a single resonance peak at about -21 ppm, indicating the presence of a sole active boron species and the absence of any decomposition products arising from the regeneration procedure. Thus, the regeneration procedure is believed to remove contaminating carbon residues while maintaining intact the important species on the catalyst surface.

20

TABLE 1					
Cycle #		C ₈ ,wt.%	C ₁₂ ⁺ ,wt%	Octane, (R+ M)/2	
5	1	initial	95.3	2.4	97.6
		final	92.2	4.9	96.1
	2	initial	95.3	2.6	97.6
		final	85.8	9.8	94.6
10	3	initial	96.8	2.0	97.5
		final	87.4	8.9	94.9
	4	initial	95.4	2.2	97.7
		final	90.9	6.5	95.7
	5	initial	96.1	1.7	97.8
		final	92.4	5.0	96.1
15	6	initial	95.8	2.1	97.8
		final	93.5	4.4	96.2
	7	initial	95.1	2.8	97.7
		final	93.4	4.5	96.3
	8	initial	94.9	2.9	97.7
		final	93.4	4.3	96.3
20	9	initial	94.3	3.1	97.5

Example 2

25 This example demonstrates the SO₂ regeneration step using a commercial MTBE raffinate feedstock which had been hydroisomerized to remove butadiene and to convert a portion of the butene-1 to cis- and trans-2-butene-2. This feedstock has the following composition (in wt% on a total olefin basis): 4.3% isobutene, 4.9% butene-1, 87.2% cis- and trans-butene-2, 1.9% 2-methyl butene-1 and 2-methyl butene-2, and 1.7% pentene-2.

30

This olefinic feedstock was blended with isobutane to a final isobutane/olefin ratio of 6. Normal butane was added to produce a level of 18% in the total feed. This feedstock was fed to the catalyst at 0°C at a WHSV (on olefin) of 7.2. Samples were taken periodically and analyzed by gas chromatography.

The catalyst was run for a total of five cycles with regeneration between cycles using liquid SO₂ in the procedure shown in Example 1. The C₈, C₁₂⁺, and (R+M)/2 values measured at the beginning and at the end of each cycle are shown in Table 2. This example shows that the regeneration step using SO₂ performs well on an alkylation catalyst which has been used on a commercial feed.

TABLE 2				
Cycle #		C ₈	C ₁₂ ⁺	Octane (R+M)/2
1	initial	77.0	6.6	95.3
	final	40.4	26.4	85.9
2	initial	79.7	6.8	95.6
	final	37.9	22.3	85.1
3	initial	81.5	6.0	95.5
	final	60.5	15.3	91.5
4	initial	79.7	5.5	95.7
	final	67.7	17.2	92.2
5	initial	82.8	4.5	95.8

It should be clear that one having ordinary skill in this art would envision equivalents to the processes found in the claims that follow and that those equivalents would be within the scope and spirit of the claimed invention.

WE CLAIM AS OUR INVENTION:

- 5 1. A method for regenerating an acidic, solid, hydrocarbon conversion catalyst which does not contain a significant Lewis acid component comprising the steps of:
- a. separating the acidic, solid, hydrocarbon conversion catalyst from a hydrocarbon conversion reaction medium,
- 10 b. contacting the acidic, solid, hydrocarbon conversion catalyst with a solvent selected from SO₂; oxygenates, alkylnitriles, and phenolics and
- c. separating the catalyst component from the solvent.
- 15 2. The process of claim 1 where the catalyst is selected from acidic zeolites, alumina, silica-alumina, silica, aluminum phosphate molecular sieves, silicoaluminophosphate molecular sieves, solid polymeric ion exchange resins, tetravalent metal phosphonates with pendent acid groups, and sulfated metal oxides.
- 20 3. The process of claim 2 where the catalyst is selected from zeolites, alumina, silica-alumina, and silica.
4. The process of claim 3 where the catalyst comprises alumina.
- 25 5. The process of claim 2 where the solvent comprises SO₂.
6. The process of claim 1 additionally comprising the step of heating the solid catalyst to a temperature of up to about 75°C
- 30 after the separation step to substantially remove volatile hydrocarbons.

7. A method for regenerating an acidic, solid, hydrocarbon conversion catalyst additionally containing a Lewis acid component comprising the steps of:
- 5 a. separating the acidic, solid, hydrocarbon conversion catalyst from a hydrocarbon conversion reaction medium,
- b. contacting the acidic, solid, hydrocarbon conversion catalyst with a solvent selected from
- 10 SO₂ and phenolics and aromatic ethers, and
- c. separating the catalyst component from the solvent.
8. The process of claim 7 where the catalyst is selected from acidic
- 15 zeolites, alumina, silica-alumina, silica, aluminum phosphate molecular sieves, silicoaluminophosphate molecular sieves, solid polymeric ion exchange resins, tetravalent metal phosphonates with pendent acid groups, and sulfated metal oxides.
9. The process of claim 8 where the catalyst is selected from
- 20 zeolites, alumina, silica-alumina, and silica.
10. The process of claim 9 where the catalyst comprises alumina.
11. The process of claim 8 where the catalyst comprises a strong
- 25 Lewis acid selected from BF₃, BCl₃, BBr₃, BI₃, SbF₅, AlCl₃, AlBr₃, TiBr₄, TiCl₄, TiCl₃, ZrCl₄, PF₅, FeCl₃, and FeBr₃.
12. The process of claim 11 where the strong Lewis acid is selected
- 30 from SbF₅, AlCl₃, and BF₃.
13. The process of claim 12 where the strong Lewis acid is BF₃.

14. The process of claim 8 where the solvent comprises SO₂.
15. The process of claim 7 additionally comprising the step of heating the solid catalyst to a temperature of up to about 75°C after the separation step to substantially remove volatile hydrocarbons.
16. A method for regenerating an alkylation catalyst component which component comprises a major amount of a transition alumina which has been contacted with a strong Lewis acid to produce an alkylation catalyst component containing between 0.5% and 30% by weight of Lewis acid and has been partially deactivated by use in an alkylation reaction medium, comprising the steps of:
- separating the alkylation catalyst from the alkylation reaction medium,
 - contacting the alkylation alumina catalyst component with a solvent comprising SO₂, and
 - separating the alkylation alumina catalyst component from the SO₂ solvent.
17. The process of claim 16 where the transition alumina is selected from gamma-alumina, eta-alumina, theta-alumina, chi-alumina, rho-alumina, and mixtures.
18. The process of claim 17 where the transition alumina is selected from gamma-alumina, eta-alumina, and mixtures.
19. The process of claim 16 where the strong Lewis acid is selected from BF₃, BCl₃, BBr₃, BI₃, SbF₅, AlCl₃, AlBr₃, TiBr₄, TiCl₄, TiCl₃, ZrCl₄, PF₅, FeCl₃, and FeBr₃.

5

10

15

20

25

30

20. The process of claim 19 where the strong Lewis acid is selected from SbF_5 , AlCl_3 , and BF_3 .
21. The process of claim 20 where the strong Lewis acid is BF_3 .
22. The process of claim 16 additionally comprising the step of heating the alkylation catalyst component to a temperature of up to about 75°C after the separation step to substantially remove volatile hydrocarbons.
23. An alkylation process comprising the steps of:
- contacting a mixture comprising isoparaffins and n-olefins with an acidic alkylation catalyst system comprising a catalyst system comprising i.) a solid catalyst component of a transition alumina or zeolite which has been previously contacted with a Lewis acid, and ii.) free Lewis acid, under alkylation conditions to produce an alkylate stream,
 - separating the alkylate stream from the solid alkylation catalyst system,
 - contacting the solid alkylation catalyst with a solvent comprising SO_2 ,
 - separating the solid alkylation catalyst component from the SO_2 solvent, and
 - recycling the solid alkylation catalyst component to the alkylation step.
24. The process of claim 23 where the solid alkylation catalyst comprises one or more of gamma-alumina, eta-alumina, theta-alumina, chi-alumina, rho-alumina, and mixtures.

25. The process of claim ²⁷24 where the transition alumina is gamma-alumina, eta-alumina, or mixtures.
- 5 26. The process of claim 23 where the strong Lewis acid is selected from BF_3 , BCl_3 , BBr_3 , BI_3 , SbF_5 , AlCl_3 , AlBr_3 , TiBr_4 , TiCl_4 , TiCl_3 , ZrCl_4 , PF_5 , FeCl_3 , and FeBr_3 .
- 10 27. The process of claim 26 where the strong Lewis acid is selected from SbF_5 , AlCl_3 , and BF_3 .
- 15 28. The process of claim 27 where the strong Lewis acid is BF_3 .
- 20 29. The process of claim 28 where the BF_3 is contacted with the solid alkylation catalyst at a pressure above the pressure of the reaction before the catalyst is recycled.
30. The process of claim 23 additionally comprising the step of heating the solid alkylation catalyst component to a temperature of up to about 75°C after the separation step to substantially remove volatile hydrocarbons.
- 25 31. The process of claim 23 where alkylation conditions include a temperature in the range of -30°C to 50°C .
32. The process of claim 23 where the mixture comprises 2-butene and isoparaffin.
- 30 33. The process of claim 23 including the step of mixing the alkylate stream with other hydrocarbons to produce a gasoline blending component or gasoline.

1/2

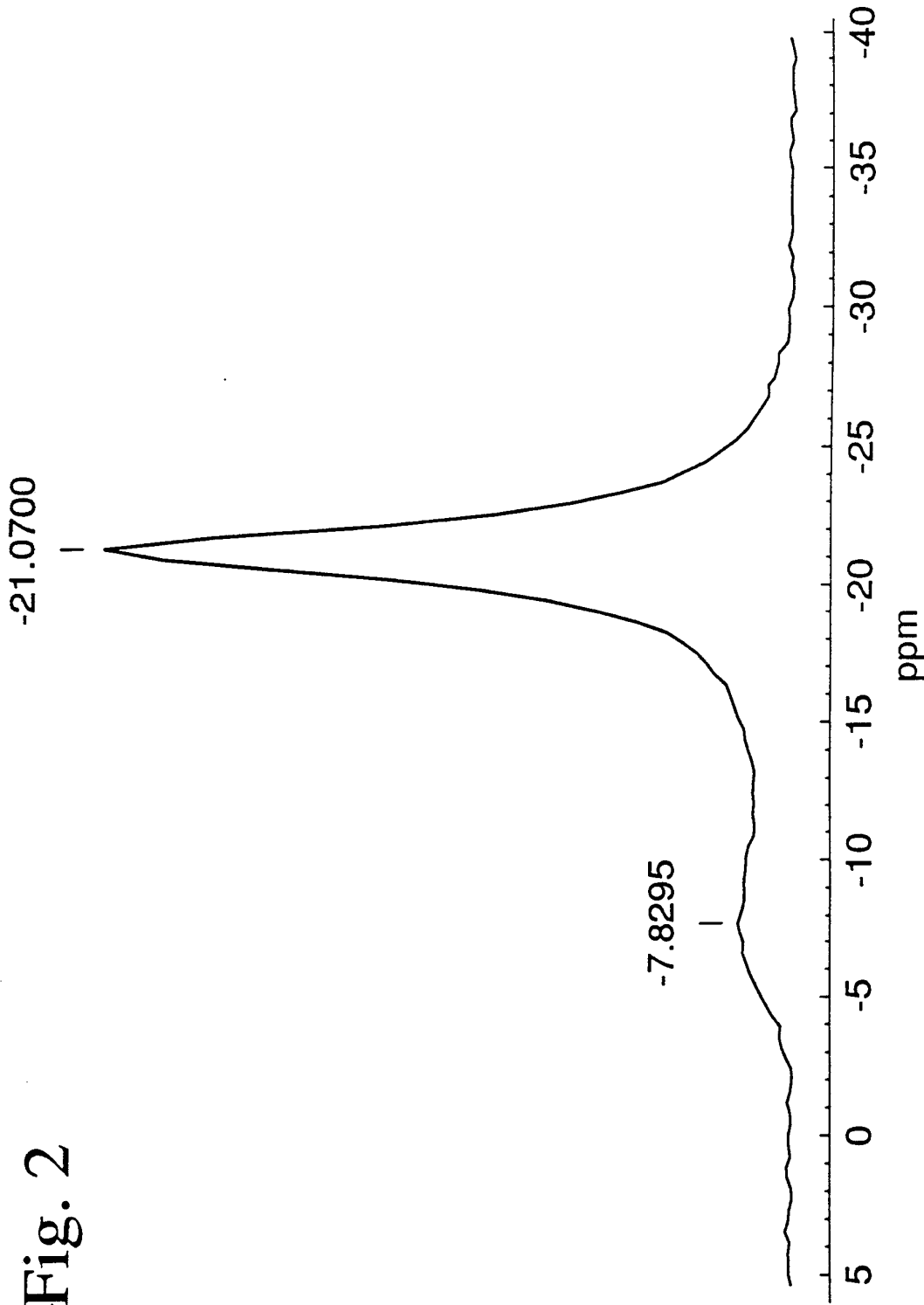
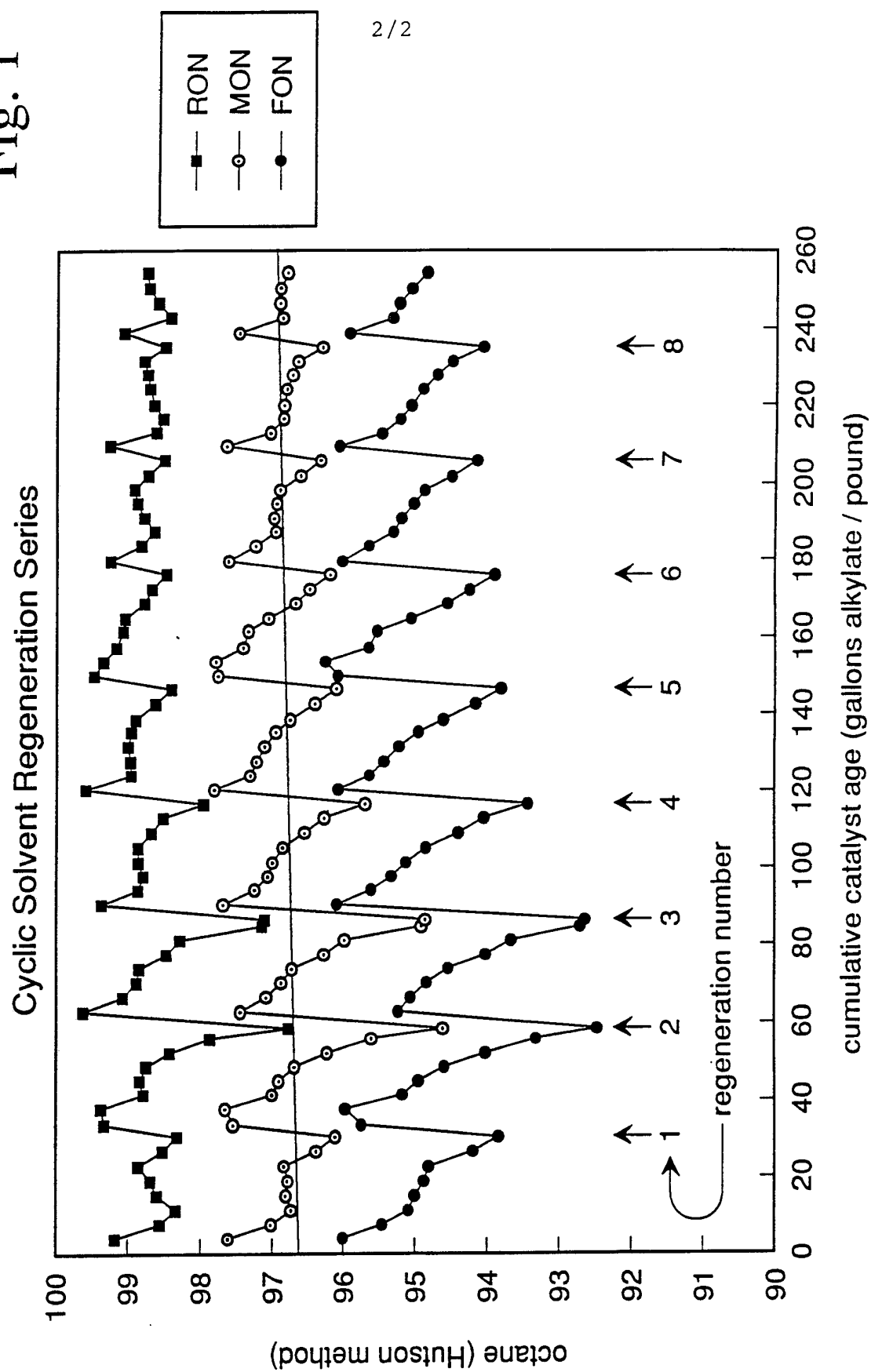


Fig. 1



INTERNATIONAL SEARCH REPORT

PCT/US92/10095

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :C07C 2/56, 2/58; B01J 20/34, 38/48, 38/50, 38/52

US CL :585/709,721,722,725,726,727,728; 502/22,29,33

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)

U.S. : 585/709,721,722,725,726,727,728; 502/22,29,33

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 practicable, 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	US,A, 2,971,037 (Gilbert et al.) 07 February 1961 See the entire document.	1-33
A	US,A, 4,066,716 (Herbstman et al.) 03 January 1978 See the entire document.	1-33
Y	US,A, 4,028,430 (Stine et al.) 07 June 1977 See column 5, lines 15-20 and column 13.	7-33
X	US,A, 3,647,916 (Caesar et al.) 07 March 1972 See column 8, lines 44-51.	1-3 and 6
A	US,A, 2,972,649 (Thomas et al.) 21 February 1961 See the entire document.	1-33

☒ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

* Special categories of cited documents:	"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
"A" document defining the general state of the art which is not considered to be part of particular relevance	"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
"E" earlier document published on or after the international filing date	"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
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Z" document member of the same patent family
"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	

Date of the actual completion of the international search 19 JANUARY 1991	Date of mailing of the international search report 16 FEB 1993
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. NOT APPLICABLE	Authorized officer <i>my meaus</i> R.D. IRZINSKI Telephone No. (703) 308-3802

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US92/10095

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A, 4,243,550 (Burk et al.) 06 January 1981 See column 7, lines 37-45.	1-3 and 5-6
Y	ACS Symposium Series 411, American Chemical Society Washington, D.C., 1989, Seapan et al. "Decoking and Regeneration of a Hydrotreating Catalyst by Supercritical Extraction", pp. 79-89. See page 81.	7-33
A	US,A, 4,992,615 (Huss, Jr. et al.) 12 February 1991 See the entire document.	1-33