



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification <sup>6</sup> : C01B 39/48, 39/08, 39/12, 37/02, B01J 29/70, 29/86, 29/87, C10G 45/64, 65/04, 65/12, 35/095, C07C 2/66, 6/12, 5/41, 5/22, 5/27, 2/12, C10G 50/00, 3/00, B01D 53/047</p>	A1	<p>(11) International Publication Number: <b>WO 99/08961</b></p> <p>(43) International Publication Date: 25 February 1999 (25.02.99)</p>
<p>(21) International Application Number: PCT/US98/16401</p> <p>(22) International Filing Date: 10 August 1998 (10.08.98)</p> <p>(30) Priority Data: 08/910,770 13 August 1997 (13.08.97) US 09/119,806 21 July 1998 (21.07.98) US</p> <p>(71) Applicant: CALIFORNIA INSTITUTE OF TECHNOLOGY [US/US]; 1200 East California Boulevard, Pasadena, CA 91125 (US).</p> <p>(72) Inventors: DAVIS, Mark, E.; 575 Laguna Road, Pasadena, CA 91105 (US). YOSHIKAWA, Masahito; 1-82-B-2-1, Ikegamidai, Midori-ku, Nagoya 458 (JP).</p> <p>(74) Agents: SHERIDAN, Richard, J. et al.; Chevron Corporation, Law Dept., P.O. Box 7141, San Francisco, CA 94120-7141 (US).</p>	<p>(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</p> <p><b>Published</b> <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>	
<p>(54) Title: ZEOLITE CIT-5</p> <p>(57) Abstract</p> <p>The present invention relates to new crystalline zeolite CIT-5 prepared using a N(16) methylsparteinium cation templating agent.</p>		

*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.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

## 1 ZEOLITE CIT-5

2 This application is a continuation-in-part of application Serial No. 08/910,770, filed  
3 August 13, 1997 which is incorporated herein by reference.

4 BACKGROUND OF THE INVENTION5 Field of the Invention

6 The present invention relates to new crystalline zeolite CIT-5, a method for  
7 preparing CIT-5 using a N(16) methylsperinium cation templating agent, and processes  
8 employing CIT-5 as a catalyst.

9 State of the Art

10 Because of their unique sieving characteristics, as well as their catalytic properties,  
11 crystalline molecular sieves and zeolites are especially useful in applications such as  
12 hydrocarbon conversion, gas drying and separation. Although many different crystalline  
13 molecular sieves have been disclosed, there is a continuing need for new zeolites with  
14 desirable properties for gas separation and drying, hydrocarbon and chemical conversions,  
15 and other applications. New zeolites may contain novel internal pore architectures,  
16 providing enhanced selectivities in these processes.

17 SUMMARY OF THE INVENTION

18 The present invention is directed to a family of crystalline molecular sieves with  
19 unique properties, referred to herein as "zeolite CIT-5" or simply "CIT-5". Preferably, CIT-  
20 5 is obtained in its silicate or aluminosilicate form. The term "silicate" refers to a zeolite  
21 having a high mole ratio of silicon oxide relative to aluminum oxide, preferably a mole ratio  
22 greater than about 100. As used herein, the term "aluminosilicate" refers to a zeolite  
23 containing both alumina and silica.

24 In accordance with this invention, there is provided a zeolite comprising an oxide of  
25 a tetravalent element or mixture of oxides of tetravalent elements and, optionally, an oxide  
26 of a trivalent element or mixtures of oxides of trivalent elements and having, after  
27 calcination, the X-ray diffraction lines of Table II.

28 Further, in accordance with this invention, there is provided a zeolite comprising an  
29 oxide selected from silicon oxide, germanium oxide and mixtures thereof and an optional  
30 oxide selected from aluminum oxide, boron oxide, gallium oxide, iron oxide and mixtures  
31 thereof and having, after calcination, the X-ray diffraction lines of Table II below.

32 The present invention further provides such a zeolite having a composition, as

1 synthesized and in the anhydrous state, in terms of mole ratios as follows:

2  $YO_2/W_aO_b > 40$

3  $M/YO_2 \leq 0.05$

4  $Q/YO_2 \leq 0.05$

5 wherein Y is silicon, germanium or a mixture thereof; W is aluminum, boron, gallium, iron  
6 or mixtures thereof; a= 1 or 2, b=2 when a=1 (i.e., W is tetravalent) and b=3 when a=2 (i.e.,  
7 W is trivalent); M is an alkali metal; and Q comprises a N(16) methylsperinium cation.

8 In accordance with this invention, there is provided a zeolite comprising an oxide of  
9 silicon, germanium or mixtures thereof and an oxide of titanium and having, after  
10 calcination, the X-ray diffraction lines of Table II.

11 The present invention also provides a zeolite having a composition, as synthesized  
12 and in the anhydrous state, in terms of mole ratios as follows:

13  $YO_2/TiO_2 > 40$

14  $M/YO_2 \leq 0.05$

15  $Q/YO_2 \leq 0.05$

16 wherein Y is silicon, germanium or a mixture thereof; M is an alkali metal; and Q  
17 comprises a N(16) methylsperinium cation.

18 In accordance with this invention, there is also provided a zeolite prepared by  
19 thermally treating a zeolite comprising an oxide selected from silicon oxide, germanium  
20 oxide and mixtures thereof and, optionally, an oxide selected from aluminum oxide, boron  
21 oxide, gallium oxide, iron oxide and mixtures thereof at a temperature of from about 200°C  
22 to about 800°C, the thus-prepared zeolite having the X-ray diffraction lines of Table II. The  
23 present invention also includes this thus-prepared zeolite which is predominantly in the  
24 hydrogen form, which hydrogen form is prepared by ion exchanging with an acid or with a  
25 solution of an ammonium salt followed by a second calcination.

26 Also provided in accordance with the present invention is a method of preparing a  
27 crystalline material comprising an oxide of a tetravalent element or mixture of oxides of  
28 tetravalent elements and, optionally, an oxide of a trivalent element or mixtures of oxides of  
29 trivalent elements, said method comprising contacting in admixture under crystallization  
30 conditions sources of said oxides, a source of alkali metal and a templating agent comprising  
31 a N(16) methylsperinium cation.

32 The present invention additionally provides a process for converting hydrocarbons

1 comprising contacting a hydrocarbonaceous feed at hydrocarbon converting conditions with  
2 a catalyst comprising the zeolite of this invention. The zeolite may be predominantly in the  
3 hydrogen form, partially acidic or substantially free of acidity, depending on the process.

4 Further provided by the present invention is a hydrocracking process comprising  
5 contacting a hydrocarbon feedstock under hydrocracking conditions with a catalyst  
6 comprising the zeolite of this invention, preferably predominantly in the hydrogen form.

7 This invention also includes a dewaxing process comprising contacting a  
8 hydrocarbon feedstock under dewaxing conditions with a catalyst comprising the zeolite of  
9 this invention, preferably predominantly in the hydrogen form.

10 The present invention also includes a process for improving the viscosity index of a  
11 dewaxed product of waxy hydrocarbon feeds comprising contacting the waxy hydrocarbon  
12 feed under isomerization dewaxing conditions with a catalyst comprising the zeolite of this  
13 invention, preferably predominantly in the hydrogen form.

14 The present invention further includes a process for producing a C<sub>20+</sub> lube oil from a  
15 C<sub>20+</sub> olefin feed comprising isomerizing said olefin feed under isomerization conditions over  
16 a catalyst comprising at least one Group VIII metal and the zeolite of this invention. The  
17 zeolite may be predominantly in the hydrogen form.

18 In accordance with this invention, there is also provided a process for catalytically  
19 dewaxing a hydrocarbon oil feedstock boiling above about 350°F and containing straight  
20 chain and slightly branched chain hydrocarbons comprising contacting said hydrocarbon oil  
21 feedstock in the presence of added hydrogen gas at a hydrogen pressure of about 15-3000 psi  
22 with a catalyst comprising at least one Group VIII metal and the zeolite of this invention,  
23 preferably predominantly in the hydrogen form. The catalyst may be a layered catalyst  
24 comprising a first layer comprising at least one Group VIII metal and the zeolite of this  
25 invention, and a second layer comprising an aluminosilicate zeolite which is more shape  
26 selective than the zeolite of said first layer.

27 Also included in the present invention is a process for preparing a lubricating oil  
28 which comprises hydrocracking in a hydrocracking zone a hydrocarbonaceous feedstock to  
29 obtain an effluent comprising a hydrocracked oil, and catalytically dewaxing said effluent  
30 comprising hydrocracked oil at a temperature of at least about 400°F and at a pressure of  
31 from about 15 psig to about 3000 psig in the presence of added hydrogen gas with a catalyst  
32 comprising at least one Group VIII metal and the zeolite of this invention. The zeolite may

1 be predominantly in the hydrogen form.

2 Further included in this invention is a process for isomerization dewaxing a raffinate  
3 comprising contacting said raffinate in the presence of added hydrogen with a catalyst  
4 comprising at least one Group VIII metal and the zeolite of this invention. The raffinate  
5 may be bright stock, and the zeolite may be predominantly in the hydrogen form.

6 Also included in this invention is a process for increasing the octane of a  
7 hydrocarbon feedstock to produce a product having an increased aromatics content  
8 comprising contacting a hydrocarbonaceous feedstock which comprises normal and slightly  
9 branched hydrocarbons having a boiling range above about 40°C and less than about 200°C,  
10 under aromatic conversion conditions with a catalyst comprising the zeolite of this invention  
11 made substantially free of acidity by neutralizing said zeolite with a basic metal. Also  
12 provided in this invention is such a process wherein the zeolite contains a Group VIII metal  
13 component.

14 Also provided by the present invention is a catalytic cracking process comprising  
15 contacting a hydrocarbon feedstock in a reaction zone under catalytic cracking conditions in  
16 the absence of added hydrogen with a catalyst comprising the zeolite of this invention,  
17 preferably predominantly in the hydrogen form. Also included in this invention is such a  
18 catalytic cracking process wherein the catalyst additionally comprises a large pore crystalline  
19 cracking component.

20 This invention further provides an isomerization process for isomerizing C<sub>4</sub> to C<sub>7</sub>  
21 hydrocarbons, comprising contacting a feed having normal and slightly branched C<sub>4</sub> to C<sub>7</sub>  
22 hydrocarbons under isomerizing conditions with a catalyst comprising the zeolite of this  
23 invention, preferably predominantly in the hydrogen form. The zeolite may be impregnated  
24 with at least one Group VIII metal, preferably platinum. The catalyst may be calcined in a  
25 steam/air mixture at an elevated temperature after impregnation of the Group VIII metal.

26 Also provided by the present invention is a process for alkylating an aromatic  
27 hydrocarbon which comprises contacting under alkylation conditions at least a molar excess  
28 of an aromatic hydrocarbon with a C<sub>2</sub> to C<sub>20</sub> olefin under at least partial liquid phase  
29 conditions and in the presence of a catalyst comprising the zeolite of this invention,  
30 preferably predominantly in the hydrogen form. The olefin may be a C<sub>2</sub> to C<sub>4</sub> olefin, and the  
31 aromatic hydrocarbon and olefin may be present in a molar ratio of about 4:1 to about 20:1,  
32 respectively. The aromatic hydrocarbon may be selected from the group consisting of

1 benzene, toluene, ethylbenzene, xylene, or mixtures thereof.

2 Further provided in accordance with this invention is a process for transalkylating an  
3 aromatic hydrocarbon which comprises contacting under transalkylating conditions an  
4 aromatic hydrocarbon with a polyalkyl aromatic hydrocarbon under at least partial liquid  
5 phase conditions and in the presence of a catalyst comprising the zeolite of this invention,  
6 preferably predominantly in the hydrogen form. The aromatic hydrocarbon and the  
7 polyalkyl aromatic hydrocarbon may be present in a molar ratio of from about 1:1 to about  
8 25:1, respectively. The aromatic hydrocarbon may be selected from the group consisting of  
9 benzene, toluene, ethylbenzene, xylene, or mixtures thereof, and the polyalkyl aromatic  
10 hydrocarbon may be a dialkylbenzene.

11 Further provided by this invention is a process to convert paraffins to aromatics  
12 which comprises contacting paraffins under conditions which cause paraffins to convert to  
13 aromatics with a catalyst comprising the zeolite of this invention, said catalyst comprising  
14 gallium, zinc, or a compound of gallium or zinc.

15 In accordance with this invention there is also provided a process for isomerizing  
16 olefins comprising contacting said olefin under conditions which cause isomerization of the  
17 olefin with a catalyst comprising the zeolite of this invention.

18 Further provided in accordance with this invention is a process for isomerizing an  
19 isomerization feed comprising an aromatic C<sub>8</sub> stream of xylene isomers or mixtures of  
20 xylene isomers and ethylbenzene, wherein a more nearly equilibrium ratio of ortho-, meta-  
21 and para-xylenes is obtained, said process comprising contacting said feed under  
22 isomerization conditions with a catalyst comprising the zeolite of this invention.

23 The present invention further provides a process for oligomerizing olefins  
24 comprising contacting an olefin feed under oligomerization conditions with a catalyst  
25 comprising the zeolite of this invention.

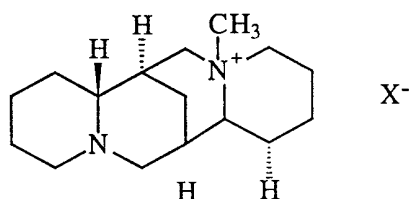
26 This invention also provides a process for converting lower alcohols and other  
27 oxygenated hydrocarbons comprising contacting said lower alcohol or other oxygenated  
28 hydrocarbon with a catalyst comprising the zeolite of this invention under conditions to  
29 produce liquid products.

30 Also provided by the present invention is an improved process for the reduction of  
31 oxides of nitrogen contained in a gas stream in the presence of oxygen wherein said process  
32 comprises contacting the gas stream with a zeolite, the improvement comprising using as the

1 zeolite, the zeolite of this invention. The zeolite may contain a metal or metal ions (such as  
2 cobalt, copper or mixtures thereof) capable of catalyzing the reduction of the oxides of  
3 nitrogen, and may be conducted in the presence of a stoichiometric excess of oxygen. In a  
4 preferred embodiment, the gas stream is the exhaust stream of an internal combustion  
5 engine.

#### 6 DETAILED DESCRIPTION OF THE INVENTION

7 In preparing CIT-5 zeolites, a N(16) methylsparteinium cation is used as a  
8 crystallization template. The N(16) methylsparteinium cation may have the following  
9 structure:



10

11 The anion (X<sup>-</sup>) associated with the cation may be any anion which is not detrimental to the  
12 formation of the zeolite. Representative anions include halogen, e.g., fluoride, chloride,  
13 bromide and iodide, hydroxide, acetate, sulfate, tetrafluoroborate, carboxylate, and the like.  
14 Hydroxide is the most preferred anion.

15 The N(16) methylsparteinium cation may be prepared as described in Lobo and  
16 Davis, "Synthesis and Characterization of Pure-Silica and Boron-Substituted SSZ-24 Using  
17 N(16) methylsparteinium Bromide as Structure-Directing Agent", *Microporous Materials* 3  
18 (1994), pp. 61-69, Elsevier.

19 In general, CIT-5 is prepared by contacting an active source of one or more oxides  
20 selected from the group consisting of alkali metal oxide, trivalent element oxide(s), and  
21 tetravalent element oxide(s) with the N(16) methylsparteinium cation templating agent.

22 CIT-5 is prepared from a reaction mixture having the composition shown in Table A  
23 below.



1 TABLE A

2 Reaction Mixture

3		Typical	Preferred (*)
4	$YO_2/W_aO_b$	15 - $\infty$	25 - $\infty$
5	OH-/YO <sub>2</sub>	0.1 - 0.5	0.2 - 0.45 (0.3)
6	Q/YO <sub>2</sub>	0.1 - 0.3	0.15 - 0.25 (0.2)
7	M/YO <sub>2</sub>	0.02 - 0.3	0.05 - 0.2 (0.1)
8	H <sub>2</sub> O/YO <sub>2</sub>	15 - 200	30 - 100 (40)

9 \*Numbers in parentheses represent quantities believed to be optimal.

10 where Y, W, a, b, M and Q are as defined above.

11 It should be emphasized that CIT-5 can be made in its all-silica form, i.e., where a  
12 source of another oxide is not intentionally added to the reaction mixture. In this case,  
13  $YO_2/W_aO_b$  would be at or near  $\infty$ .

14 In practice, CIT-5 is prepared by a process comprising:

15 (a) preparing an aqueous solution containing sources of at least one oxide  
16 capable of forming a crystalline molecular sieve and a N(16) methylsperinium  
17 cation having an anionic counterion which is not detrimental to the formation of  
18 CIT-5;

19 (b) maintaining the aqueous solution under conditions sufficient to form crystals  
20 of CIT-5; and

21 (c) recovering the crystals of CIT-5.

22 Accordingly, CIT-5 may comprise the crystalline material and the templating agent  
23 in combination with metallic and non-metallic oxides bonded in tetrahedral coordination  
24 through shared oxygen atoms to form a cross-linked three dimensional crystal structure.  
25 The metallic and non-metallic oxides comprise one or a combination of oxides of a  
26 tetravalent element(s), and, optionally, one or a combination of a trivalent element(s). The  
27 tetravalent element(s) is preferably selected from the group consisting of silicon, germanium  
28 and combinations thereof. More preferably, the tetravalent element is silicon. The trivalent  
29 element is preferably aluminum, boron, gallium, or iron. In terms of reaction speed,  
30 gallium is preferred. However, in some catalytic applications, aluminum is preferred.

31 Typical sources of aluminum oxide for the reaction mixture include aluminates,  
32 alumina, aluminum colloids, aluminum oxide coated on silica sol, hydrated alumina gels

1 such as  $\text{Al}(\text{OH})_3$  and aluminum compounds such as  $\text{AlCl}_3$  and  $\text{Al}_2(\text{SO}_4)_3$ . Typical sources  
2 of silicon oxide include silicates, silica hydrogel, silicic acid, fumed silica, colloidal silica,  
3 tetra-alkyl orthosilicates, and silica hydroxides.

4 A source zeolite reagent may provide a source of aluminum. In most cases, the  
5 source zeolite also provides a source of silica. The source zeolite in its dealuminated or  
6 form may also be used as a source of silica, with additional silicon added using, for  
7 example, the conventional sources listed above. Use of a source zeolite reagent as a source  
8 of alumina for the present process is more completely described in U.S. Patent  
9 No. 5,225,179, issued July 6, 1993 to Zones et al. entitled "Method of Making Molecular  
10 Sieves", the disclosure of which is incorporated herein by reference.

11 An alkali metal is added to the reaction mixture. A variety of sources can be used,  
12 such as alkali metal hydroxides and alkali metal carbonates. Lithium or a mixture of lithium  
13 and another alkali metal is preferred, with lithium hydroxide being particularly preferred.  
14 The lithium cation may be part of the as-synthesized crystalline oxide material, in order to  
15 balance valence electron charges therein. Other alkali metals which can be used include  
16 sodium and potassium, with the hydroxides being preferred. The alkali metal may be  
17 employed in an amount of from about 0.03 to about 0.15 mole of alkali metal per mole of  
18 silica (or other oxide(s) of a tetravalent element(s)).

19 It has been found that the inclusion of zinc in the reaction mixture can help prevent  
20 the formation of crystal phases other than the CIT-5. The zinc can be added as, e.g., zinc  
21 acetate dihydrate, in an amount of up to about 0.08, preferably about 0.04, mole of zinc  
22 acetate dihydrate per mole of silica (or other oxide(s) of a tetravalent element(s)).

23 The reaction mixture is maintained at an elevated temperature until the crystals of  
24 the CIT-5 zeolite are formed. The hydrothermal crystallization is usually conducted under  
25 autogenous pressure, at a temperature between  $100^\circ\text{C}$  and  $200^\circ\text{C}$ , preferably between  $135^\circ\text{C}$   
26 and  $160^\circ\text{C}$ . The crystallization period is typically greater than 1 day and preferably from  
27 about 7 days to about 21 days.

28 During the hydrothermal crystallization step, the CIT-5 crystals can be allowed to  
29 nucleate spontaneously from the reaction mixture. The use of CIT-5 crystals as seed  
30 material can be advantageous in decreasing the time necessary for complete crystallization  
31 to occur. In addition, seeding can lead to an increased purity of the product obtained by  
32 promoting the nucleation and/or formation of CIT-5 over any undesired phases. When used

1 as seeds, CIT-5 crystals are added in an amount between 0.1 and 10% of the weight of silica  
2 used in the reaction mixture.

3 Once the zeolite crystals have formed, the solid product is separated from the  
4 reaction mixture by standard mechanical separation techniques such as filtration. The  
5 crystals are water-washed and then dried, e.g., at 90°C to 150°C for from 8 to 24 hours, to  
6 obtain the as-synthesized CIT-5 zeolite crystals. The drying step can be performed at  
7 atmospheric pressure or under vacuum.

8 CIT-5 has a composition, as synthesized and in the anhydrous state, in terms of mole  
9 ratios, shown in Table B below.

10 TABLE B

11 As-Synthesized CIT-5

12	$YO_2/W_aO_b$	> 40
13	$M/YO_2$	$\leq 0.05$
14	$Q/YO_2$	$\leq 0.05$

15 where Y, W, a, b, M and Q are as defined above. As noted above, CIT-5 can be in the all-  
16 silica form, in which case  $YO_2/W_aO_b$  would be at or near  $\infty$ .

17 Lower silica to alumina ratios may also be obtained by using methods which insert  
18 aluminum into the crystalline framework. For example, aluminum insertion may occur by  
19 thermal treatment of the zeolite in combination with an alumina binder or dissolved source  
20 of alumina. Such procedures are described in U.S. Patent No. 4,559,315, issued on  
21 December 17, 1985 to Chang et al.

22 It is believed that CIT-5 is comprised of a new framework structure or topology  
23 which is characterized by its X-ray diffraction pattern. CIT-5 zeolites, as-synthesized, have  
24 a crystalline structure whose X-ray powder diffraction pattern typically exhibits the  
25 characteristic lines shown in Table I and are thereby distinguished from other known  
26 zeolites.

1

TABLE I

2

As-Synthesized All-Silica CIT-5

<u>2 Theta</u> <sup>(a)</sup>	<u>d</u>	<u>Relative Intensity</u> <sup>(b)</sup>
6.96	12.7	VS
7.29	12.12	S
12.81	6.905	W
13.93	6.353	M
18.96	4.676	S
19.59	4.528	M
20.00	4.436	S
20.50	4.329	M-S
20.95	4.236	S-VS
21.93	4.050	W
23.41	3.797	W
24.22	3.672	W
24.62	3.612	M
25.80	3.451	W
26.10	3.412	W
26.73	3.332	S-VS
27.11	3.286	W
28.22	3.159	M
29.38	3.038	W
29.82	2.994	W
31.37	2.849	W
31.55	2.833	W
32.99	2.713	W
33.98	2.636	W
35.33	2.538	W
35.64	2.517	W
36.42	2.465	W
37.03	2.426	W
37.70	2.384	W
38.73	2.323	W
44.70	2.026	W



	24.6	3.62	5-45
	26.8	3.32	10-70
1	<sup>(a)</sup> ± 0.15		

2 The X-ray powder diffraction patterns were determined by standard techniques. The  
3 radiation was the K-alpha/doublet of copper. The peak heights and the positions, as a  
4 function of  $2\theta$  where  $\theta$  is the Bragg angle, were read from the relative intensities of the  
5 peaks, and  $d$ , the interplanar spacing in Angstroms corresponding to the recorded lines, can  
6 be calculated.

7 The variation in the scattering angle (two theta) measurements, due to instrument  
8 error and to differences between individual samples, is estimated at  $\pm 0.15$  degrees.

9 The X-ray diffraction pattern of Table I is representative of "as-synthesized" or  
10 "as-made" CIT-5 zeolites. Minor variations in the diffraction pattern can result from  
11 variations in the, e.g., silica-to-alumina mole ratio of the particular sample due to changes in  
12 lattice constants. In addition, sufficiently small crystals will affect the shape and intensity of  
13 peaks, leading to significant peak broadening.

14 Representative peaks from the X-ray diffraction pattern of calcined CIT-5 are shown  
15 in Table II. Calcination can also result in changes in the intensities of the peaks as  
16 compared to patterns of the "as-made" material, as well as minor shifts in the diffraction  
17 pattern. The zeolite produced by exchanging the metal or other cations present in the zeolite  
18 with various other cations (such as  $H^+$  or  $NH_4^+$ ) yields essentially the same diffraction  
19 pattern, although again, there may be minor shifts in the interplanar spacing and variations  
20 in the relative intensities of the peaks. Notwithstanding these minor perturbations, the basic  
21 crystal lattice remains unchanged by these treatments.

22 Crystalline CIT-5 can be used as-synthesized, but preferably will be thermally treated  
23 (calcined). Usually, it is desirable to remove the alkali metal cation by ion exchange and  
24 replace it with hydrogen, ammonium, or any desired metal ion. The zeolite can be leached  
25 with chelating agents, e.g., EDTA or dilute acid solutions, to increase the silica to alumina  
26 mole ratio. The zeolite can also be steamed; steaming helps stabilize the crystalline lattice  
27 to attack from acids.

28 The zeolite can be used in intimate combination with hydrogenating components,  
29 such as tungsten, vanadium molybdenum, rhenium, nickel cobalt, chromium, manganese, or  
30 a noble metal, such as palladium or platinum, for those applications in which a

1 hydrogenation-dehydrogenation function is desired.

2 Metals may also be introduced into the zeolite by replacing some of the cations in  
3 the zeolite with metal cations via standard ion exchange techniques (see, for example, U.S.  
4 Patent Nos. 3,140,249 issued July 7, 1964 to Plank et al.; 3,140,251 issued July 7, 1964 to  
5 Plank et al.; and 3,140,253 issued July 7, 1964 to Plank et al.). Typical replacing cations  
6 can include metal cations, e.g., rare earth, Group IA, Group IIA and Group VIII metals, as  
7 well as their mixtures. Of the replacing metallic cations, cations of metals such as rare  
8 earth, Mn, Ca, Mg, Zn, Cd, Pt, Pd, Ni, Co, Ti, Al, Sn, and Fe are particularly preferred.

9 The hydrogen, ammonium, and metal components can be ion-exchanged into the  
10 CIT-5. The zeolite can also be impregnated with the metals, or, the metals can be physically  
11 and intimately admixed with the zeolite using standard methods known to the art.

12 Typical ion-exchange techniques involve contacting the synthetic zeolite with a  
13 solution containing a salt of the desired replacing cation or cations. Although a wide variety  
14 of salts can be employed, chlorides and other halides, acetates, nitrates, and sulfates are  
15 particularly preferred. The zeolite is usually calcined prior to the ion-exchange procedure to  
16 remove the organic matter present in the channels and on the surface, since this results in a  
17 more effective ion exchange. Representative ion exchange techniques are disclosed in a  
18 wide variety of patents including U.S. Patent Nos. 3,140,249 issued on July 7, 1964 to Plank  
19 et al.; 3,140,251 issued on July 7, 1964 to Plank et al.; and 3,140,253 issued on July 7, 1964  
20 to Plank et al.

21 Following contact with the salt solution of the desired replacing cation, the zeolite is  
22 typically washed with water and dried at temperatures ranging from 65°C to about 200°C.  
23 After washing, the zeolite can be calcined in air or inert gas at temperatures ranging from  
24 about 200°C to about 800°C for periods of time ranging from 1 to 48 hours, or more, to  
25 produce a catalytically active product especially useful in hydrocarbon conversion processes.

26 Regardless of the cations present in the synthesized form of CIT-5, the spatial  
27 arrangement of the atoms which form the basic crystal lattice of the zeolite remains  
28 essentially unchanged.

29 CIT-5 can be formed into a wide variety of physical shapes. Generally speaking, the  
30 zeolite can be in the form of a powder, a granule, or a molded product, such as extrudate  
31 having a particle size sufficient to pass through a 2-mesh (Tyler) screen and be retained on a  
32 400-mesh (Tyler) screen. In cases where the catalyst is molded, such as by extrusion with

1 an organic binder, the aluminosilicate can be extruded before drying, or, dried or partially  
2 dried and then extruded.

3 CIT-5 can be composited with other materials resistant to the temperatures and other  
4 conditions employed in organic conversion processes. Such matrix materials include active  
5 and inactive materials and synthetic or naturally occurring zeolites as well as inorganic  
6 materials such as clays, silica and metal oxides. Examples of such materials and the manner  
7 in which they can be used are disclosed in U.S. Patent No. 4,910,006, issued May 20, 1990  
8 to Zones et al., and U.S. Patent No. 5,316,753, issued May 31, 1994 to Nakagawa, both of  
9 which are incorporated by reference herein in their entirety.

#### 10 Hydrocarbon Conversion Processes

11 CIT-5 zeolites are useful in hydrocarbon conversion reactions. Hydrocarbon  
12 conversion reactions are chemical and catalytic processes in which carbon containing  
13 compounds are changed to different carbon containing compounds. Examples of  
14 hydrocarbon conversion reactions in which CIT-5 are expected to be useful include  
15 hydrocracking, dewaxing, catalytic cracking and olefin and aromatics formation reactions.  
16 The catalysts are also expected to be useful in other petroleum refining and hydrocarbon  
17 conversion reactions such as isomerizing n-paraffins and naphthenes, polymerizing and  
18 oligomerizing olefinic or acetylenic compounds such as isobutylene and butene-1,  
19 reforming, isomerizing polyalkyl substituted aromatics (e.g., m-xylene), and  
20 disproportionating aromatics (e.g., toluene) to provide mixtures of benzene, xylenes and  
21 higher methylbenzenes and oxidation reactions. Also included are rearrangement reactions  
22 to make various naphthalene derivatives. The CIT-5 catalysts may have high selectivity, and  
23 under hydrocarbon conversion conditions can provide a high percentage of desired products  
24 relative to total products.

25 CIT-5 zeolites can be used in processing hydrocarbonaceous feedstocks.

26 Hydrocarbonaceous feedstocks contain carbon compounds and can be from many different  
27 sources, such as virgin petroleum fractions, recycle petroleum fractions, shale oil, liquefied  
28 coal, tar sand oil, synthetic paraffins from NAO, recycled plastic feedstocks and, in general,  
29 can be any carbon containing feedstock susceptible to zeolitic catalytic reactions.

30 Depending on the type of processing the hydrocarbonaceous feed is to undergo, the feed can  
31 contain metal or be free of metals, it can also have high or low nitrogen or sulfur impurities.

32 It can be appreciated, however, that in general processing will be more efficient (and the



1 catalyst more active) the lower the metal, nitrogen, and sulfur content of the feedstock.

2 The conversion of hydrocarbonaceous feeds can take place in any convenient mode,  
3 for example, in fluidized bed, moving bed, or fixed bed reactors depending on the types of  
4 process desired. The formulation of the catalyst particles will vary depending on the  
5 conversion process and method of operation.

6 Other reactions which can be performed using the catalyst of this invention  
7 containing a metal, e.g., a Group VIII metal such platinum, include  
8 hydrogenation-dehydrogenation reactions, denitrogenation and desulfurization reactions.

9 Depending upon the type of reaction which is catalyzed, the zeolite may be  
10 predominantly in the hydrogen form, partially acidic or substantially free of acidity. As used  
11 herein, "predominantly in the hydrogen form" means that, after calcination, at least 80% of  
12 the cation sites are occupied by hydrogen ions and/or rare earth ions.

13 The following table indicates typical reaction conditions which may be employed  
14 when using catalysts comprising CIT-5 in the hydrocarbon conversion reactions of this  
15 invention. Preferred conditions are indicated in parentheses.

Process	Temp., °C	Pressure	LHSV
Hydrocracking	175-485	0.5-350 bar	0.1-30
Dewaxing	200-475 (250-450)	15-3000 psig (200-3000)	0.1-20 (0.2-10)
Aromatics formation	400-600 (480-550)	atm.-10 bar	0.1-15
Cat. cracking	127-885	subatm. <sup>1</sup> (atm.-5 atm.)	0.5-50
Oligomerization	232-649 <sup>2</sup> 10-232 <sup>4</sup> (27-204) <sup>4</sup>	0.1-50 atm. <sup>2,3</sup> - -	0.2-50 <sup>2</sup> 0.05-20 <sup>5</sup> (0.1-10) <sup>5</sup>
Paraffins to aromatics	100-700	0-1000 psig	0.5-40 <sup>5</sup>
Condensation of alcohols	260-538	0.5-1000 psig	0.5-50 <sup>5</sup>
Isomerization	93-538 (204-315)	50-1000 psig	1-10 (1-4)
Xylene isomerization	260-593 <sup>2</sup> (315-566) <sup>2</sup> 38-371 <sup>4</sup>	0.5-50 atm. <sup>2</sup> (1-5 atm) <sup>2</sup> 1-200 atm. <sup>4</sup>	0.1-100 <sup>5</sup> (0.5-50) <sup>5</sup> 0.5-50

16 <sup>1</sup> Several hundred atmospheres

17 <sup>2</sup> Gas phase reaction

18 <sup>3</sup> Hydrocarbon partial pressure

19 <sup>4</sup> Liquid phase reaction

20 <sup>5</sup> WHSV

1 Other reaction conditions and parameters are provided below.

2 Hydrocracking

3 Using a catalyst which comprises CIT-5, preferably predominantly in the hydrogen  
4 form, and a hydrogenation promoter, heavy petroleum residual feedstocks, cyclic stocks and  
5 other hydrocrackate charge stocks can be hydrocracked using the process conditions and  
6 catalyst components disclosed in the aforementioned U.S. Patent No. 4,910,006 and U.S.  
7 Patent No. 5,316,753.

8 The hydrocracking catalysts contain an effective amount of at least one  
9 hydrogenation component of the type commonly employed in hydrocracking catalysts. The  
10 hydrogenation component is generally selected from the group of hydrogenation catalysts  
11 consisting of one or more metals of Group VIB and Group VIII, including the salts,  
12 complexes and solutions containing such. The hydrogenation catalyst is preferably selected  
13 from the group of metals, salts and complexes thereof of the group consisting of at least one  
14 of platinum, palladium, rhodium, iridium, ruthenium and mixtures thereof or the group  
15 consisting of at least one of nickel, molybdenum, cobalt, tungsten, titanium, chromium and  
16 mixtures thereof. Reference to the catalytically active metal or metals is intended to  
17 encompass such metal or metals in the elemental state or in some form such as an oxide,  
18 sulfide, halide, carboxylate and the like. The hydrogenation catalyst is present in an  
19 effective amount to provide the hydrogenation function of the hydrocracking catalyst, and  
20 preferably in the range of from 0.05 to 25% by weight.

21 Dewaxing

22 CIT-5, preferably predominantly in the hydrogen form, can be used to dewax  
23 hydrocarbonaceous feeds by selectively removing straight chain paraffins. Typically, the  
24 viscosity index of the dewaxed product is improved (compared to the waxy feed) when the  
25 waxy feed is contacted with CIT-5 under isomerization dewaxing conditions.

26 The catalytic dewaxing conditions are dependent in large measure on the feed used  
27 and upon the desired pour point. Hydrogen is preferably present in the reaction zone during  
28 the catalytic dewaxing process. The hydrogen to feed ratio is typically between about 500  
29 and about 30,000 SCF/bbl (standard cubic feet per barrel), preferably about 1000 to about  
30 20,000 SCF/bbl. Generally, hydrogen will be separated from the product and recycled to the  
31 reaction zone. Typical feedstocks include light gas oil, heavy gas oils and reduced crudes  
32 boiling above about 350°F.

1           A typical dewaxing process is the catalytic dewaxing of a hydrocarbon oil feedstock  
2 boiling above about 350°F and containing straight chain and slightly branched chain  
3 hydrocarbons by contacting the hydrocarbon oil feedstock in the presence of added hydrogen  
4 gas at a hydrogen pressure of about 15-3000 psi with a catalyst comprising CIT-5 and at  
5 least one Group VIII metal.

6           The CIT-5 hydrodewaxing catalyst may optionally contain a hydrogenation  
7 component of the type commonly employed in dewaxing catalysts. See the aforementioned  
8 U.S. Patent No. 4,910,006 and U.S. Patent No. 5,316,753 for examples of these  
9 hydrogenation components.

10           The hydrogenation component is present in an effective amount to provide an  
11 effective hydrodewaxing and hydroisomerization catalyst preferably in the range of from  
12 about 0.05 to 5% by weight. The catalyst may be run in such a mode to increase  
13 isodewaxing at the expense of cracking reactions.

14           The feed may be hydrocracked, followed by dewaxing. This type of two stage  
15 process and typical hydrocracking conditions are described in U.S. Patent No. 4,921,594,  
16 issued May 1, 1990 to Miller, which is incorporated herein by reference in its entirety.

17           CIT-5 may also be utilized as a dewaxing catalyst in the form of a layered catalyst.  
18 That is, the catalyst comprises a first layer comprising zeolite CIT-5 and at least one  
19 Group VIII metal, and a second layer comprising an aluminosilicate zeolite which is more  
20 shape selective than zeolite CIT-5. The use of layered catalysts is disclosed in U.S. Patent  
21 No. 5,149,421, issued September 22, 1992 to Miller, which is incorporated by reference  
22 herein in its entirety. The layering may also include a bed of CIT-5 layered with a non-  
23 zeolitic component designed for either hydrocracking or hydrofinishing.

24           CIT-5 may also be used to dewax raffinates, including bright stock, under conditions  
25 such as those disclosed in U. S. Patent No. 4,181,598, issued January 1, 1980 to Gillespie  
26 et al., which is incorporated by reference herein in its entirety.

27           It is often desirable to use mild hydrogenation (sometimes referred to as  
28 hydrofinishing) to produce more stable dewaxed products. The hydrofinishing step can be  
29 performed either before or after the dewaxing step, and preferably after. Hydrofinishing is  
30 typically conducted at temperatures ranging from about 190°C to about 340°C at pressures  
31 from about 400 psig to about 3000 psig at space velocities (LHSV) between about 0.1 and  
32 20 and a hydrogen recycle rate of about 400 to 1500 SCF/bbl. The hydrogenation catalyst

1 employed must be active enough not only to hydrogenate the olefins, diolefins and color  
2 bodies which may be present, but also to reduce the aromatic content. Suitable  
3 hydrogenation catalyst are disclosed in U. S. Patent No. 4,921,594, issued May 1, 1990 to  
4 Miller, which is incorporated by reference herein in its entirety. The hydrofinishing step is  
5 beneficial in preparing an acceptably stable product (e.g., a lubricating oil) since dewaxed  
6 products prepared from hydrocracked stocks tend to be unstable to air and light and tend to  
7 form sludges spontaneously and quickly.

8 Lube oil may be prepared using CIT-5. For example, a C<sub>20+</sub> lube oil may be made by  
9 isomerizing a C<sub>20+</sub> olefin feed over a catalyst comprising CIT-5 in the hydrogen form and at  
10 least one Group VIII metal. Alternatively, the lubricating oil may be made by hydrocracking  
11 in a hydrocracking zone a hydrocarbonaceous feedstock to obtain an effluent comprising a  
12 hydrocracked oil, and catalytically dewaxing the effluent at a temperature of at least about  
13 400°F and at a pressure of from about 15 psig to about 3000 psig in the presence of added  
14 hydrogen gas with a catalyst comprising CIT-5 in the hydrogen form and at least one  
15 Group VIII metal.

#### 16 Aromatics Formation

17 CIT-5 can be used to convert light straight run naphthas and similar mixtures to  
18 highly aromatic mixtures. Thus, normal and slightly branched chained hydrocarbons,  
19 preferably having a boiling range above about 40°C and less than about 200°C, can be  
20 converted to products having a substantial higher octane aromatics content by contacting the  
21 hydrocarbon feed with a catalyst comprising CIT-5. It is also possible to convert heavier  
22 feeds into BTX or naphthalene derivatives of value using a catalyst comprising CIT-5.

23 The conversion catalyst preferably contains a Group VIII metal compound to have  
24 sufficient activity for commercial use. By Group VIII metal compound as used herein is  
25 meant the metal itself or a compound thereof. The Group VIII noble metals and their  
26 compounds, platinum, palladium, and iridium, or combinations thereof can be used.  
27 Rhenium or tin or a mixture thereof may also be used in conjunction with the Group VIII  
28 metal compound and preferably a noble metal compound. The most preferred metal is  
29 platinum. The amount of Group VIII metal present in the conversion catalyst should be  
30 within the normal range of use in reforming catalysts, from about 0.05 to 2.0 weight percent,  
31 preferably 0.2 to 0.8 weight percent.

32 It is critical to the selective production of aromatics in useful quantities that the

1 conversion catalyst be substantially free of acidity, for example, by neutralizing the zeolite  
2 with a basic metal, e.g., alkali metal, compound. Methods for rendering the catalyst free of  
3 acidity are known in the art. See the aforementioned U.S. Patent No. 4,910,006 and U.S.  
4 Patent No. 5,316,753 for a description of such methods.

5 The preferred alkali metals are sodium, potassium, rubidium and cesium. The  
6 zeolite itself can be substantially free of acidity only at very high silica:alumina mole ratios.

#### 7 Catalytic Cracking

8 Hydrocarbon cracking stocks can be catalytically cracked in the absence of hydrogen  
9 using CIT-5, preferably predominantly in the hydrogen form.

10 When CIT-5 is used as a catalytic cracking catalyst in the absence of hydrogen, the  
11 catalyst may be employed in conjunction with traditional cracking catalysts, e.g., any  
12 aluminosilicate heretofore employed as a component in cracking catalysts. Typically, these  
13 are large pore, crystalline aluminosilicates. Examples of these traditional cracking catalysts  
14 are disclosed in the aforementioned U.S. Patent No. 4,910,006 and U.S. Patent  
15 No 5,316,753. When a traditional cracking catalyst (TC) component is employed, the  
16 relative weight ratio of the TC to the CIT-5 is generally between about 1:10 and about  
17 500:1, desirably between about 1:10 and about 200:1, preferably between about 1:2 and  
18 about 50:1, and most preferably is between about 1:1 and about 20:1. The novel zeolite  
19 and/or the traditional cracking component may be further ion exchanged with rare earth ions  
20 to modify selectivity.

21 The cracking catalysts are typically employed with an inorganic oxide matrix  
22 component. See the aforementioned U.S. Patent No. 4,910,006 and U.S. Patent  
23 No. 5,316,753 for examples of such matrix components.

#### 24 Isomerization

25 The present catalyst, preferably predominantly in the hydrogen form, is believed to  
26 be active and selective for isomerizing C<sub>4</sub> to C<sub>7</sub> hydrocarbons. The activity means that the  
27 catalyst can operate at relatively low temperature which thermodynamically favors highly  
28 branched paraffins. Consequently, the catalyst can produce a high octane product. The  
29 selectivity means that a relatively high liquid yield can be achieved when the catalyst is run  
30 at a high octane.

31 The present process comprises contacting the isomerization catalyst, i.e., a catalyst  
32 comprising CIT-5 in the hydrogen form, with a hydrocarbon feed under isomerization

1 conditions. The feed is preferably a light straight run fraction, boiling within the range of  
2 30°F to 250°F and preferably from 60°F to 200°F. Preferably, the hydrocarbon feed for the  
3 process comprises a substantial amount of C<sub>4</sub> to C<sub>7</sub> normal and slightly branched low octane  
4 hydrocarbons, more preferably C<sub>5</sub> and C<sub>6</sub> hydrocarbons.

5 It is preferable to carry out the isomerization reaction in the presence of hydrogen.  
6 Preferably, hydrogen is added to give a hydrogen to hydrocarbon ratio (H<sub>2</sub>/HC) of between  
7 0.5 and 10 H<sub>2</sub>/HC, more preferably between 1 and 8 H<sub>2</sub>/HC. See the aforementioned U.S.  
8 Patent No. 4,910,006 and U.S. Patent No. 5,316,753 for a further discussion of  
9 isomerization process conditions.

10 A low sulfur feed is especially preferred in the present process. The feed preferably  
11 contains less than 10 ppm, more preferably less than 1 ppm, and most preferably less than  
12 0.1 ppm sulfur. In the case of a feed which is not already low in sulfur, acceptable levels  
13 can be reached by hydrogenating the feed in a presaturation zone with a hydrogenating  
14 catalyst which is resistant to sulfur poisoning. See the aforementioned U.S. Patent  
15 No. 4,910,006 and U.S. Patent No. 5,316,753 for a further discussion of this  
16 hydrodesulfurization process.

17 It is preferable to limit the nitrogen level and the water content of the feed. Catalysts  
18 and processes which are suitable for these purposes are known to those skilled in the art.

19 After a period of operation, the catalyst can become deactivated by sulfur or coke.  
20 See the aforementioned U.S. Patent No. 4,910,006 and U.S. Patent No. 5,316,753 for a  
21 further discussion of methods of removing this sulfur and coke, and of regenerating the  
22 catalyst.

23 The conversion catalyst preferably contains a Group VIII metal compound to have  
24 sufficient activity for commercial use. By Group VIII metal compound as used herein is  
25 meant the metal itself or a compound thereof. The Group VIII noble metals and their  
26 compounds, platinum, palladium, and iridium, or combinations thereof can be used.  
27 Rhenium and tin may also be used in conjunction with the noble metal. The most preferred  
28 metal is platinum. The amount of Group VIII metal present in the conversion catalyst  
29 should be within the normal range of use in isomerizing catalysts, from about 0.05 to  
30 2.0 weight percent, preferably 0.2 to 0.8 weight percent.

### 31 Alkylation and Transalkylation

32 CIT-5 can be used in a process for the alkylation or transalkylation of an aromatic

1 hydrocarbon. The process comprises contacting the aromatic hydrocarbon with a C<sub>2</sub> to C<sub>16</sub>  
2 olefin alkylating agent or a polyalkyl aromatic hydrocarbon transalkylating agent, under at  
3 least partial liquid phase conditions, and in the presence of a catalyst comprising CIT-5.

4 CIT-5 can also be used for removing benzene from gasoline by alkylating the  
5 benzene as described above and removing the alkylated product from the gasoline.

6 For high catalytic activity, the CIT-5 zeolite should be predominantly in its hydrogen  
7 ion form. It is preferred that, after calcination, at least 80% of the cation sites are occupied  
8 by hydrogen ions and/or rare earth ions.

9 Examples of suitable aromatic hydrocarbon feedstocks which may be alkylated or  
10 transalkylated by the process of the invention include aromatic compounds such as benzene,  
11 toluene and xylene. The preferred aromatic hydrocarbon is benzene. There may be  
12 occasions where naphthalene derivatives may be desirable. Mixtures of aromatic  
13 hydrocarbons may also be employed.

14 Suitable olefins for the alkylation of the aromatic hydrocarbon are those containing 2  
15 to 20, preferably 2 to 4, carbon atoms, such as ethylene, propylene, butene-1, trans-butene-2  
16 and cis-butene-2, or mixtures thereof. There may be instances where pentenes are desirable.  
17 The preferred olefins are ethylene and propylene. Longer chain alpha olefins may be used as  
18 well.

19 When transalkylation is desired, the transalkylating agent is a polyalkyl aromatic  
20 hydrocarbon containing two or more alkyl groups that each may have from 2 to about  
21 4 carbon atoms. For example, suitable polyalkyl aromatic hydrocarbons include di-, tri- and  
22 tetra-alkyl aromatic hydrocarbons, such as diethylbenzene, triethylbenzene,  
23 diethylmethylbenzene (diethyltoluene), di-isopropylbenzene, di-isopropyltoluene,  
24 dibutylbenzene, and the like. Preferred polyalkyl aromatic hydrocarbons are the dialkyl  
25 benzenes. A particularly preferred polyalkyl aromatic hydrocarbon is di-isopropylbenzene.

26 When alkylation is the process conducted, reaction conditions are as follows. The  
27 aromatic hydrocarbon feed should be present in stoichiometric excess. It is preferred that  
28 molar ratio of aromatics to olefins be greater than four-to-one to prevent rapid catalyst  
29 fouling. The reaction temperature may range from 100°F to 600°F, preferably 250°F to  
30 450°F. The reaction pressure should be sufficient to maintain at least a partial liquid phase  
31 in order to retard catalyst fouling. This is typically 50 psig to 1000 psig depending on the  
32 feedstock and reaction temperature. Contact time may range from 10 seconds to 10 hours,

1 but is usually from 5 minutes to an hour. The weight hourly space velocity (WHSV), in  
2 terms of grams (pounds) of aromatic hydrocarbon and olefin per gram (pound) of catalyst  
3 per hour, is generally within the range of about 0.5 to 50.

4 When transalkylation is the process conducted, the molar ratio of aromatic  
5 hydrocarbon will generally range from about 1:1 to 25:1, and preferably from about 2:1 to  
6 20:1. The reaction temperature may range from about 100°F to 600°F, but it is preferably  
7 about 250°F to 450°F. The reaction pressure should be sufficient to maintain at least a  
8 partial liquid phase, typically in the range of about 50 psig to 1000 psig, preferably 300 psig  
9 to 600 psig. The weight hourly space velocity will range from about 0.1 to 10. U.S. Patent  
10 No. 5,082,990 issued on January 21, 1992 to Hsieh, et al. describes such processes and is  
11 incorporated herein by reference.

#### 12 Isomerization of Olefins

13 CIT-5 can be used to isomerize olefins. The feed stream is a hydrocarbon stream  
14 containing at least one C<sub>4-6</sub> olefin, preferably a C<sub>4-6</sub> normal olefin, more preferably normal  
15 butene. Normal butene as used in this specification means all forms of normal butene, e.g.,  
16 1-butene, cis-2-butene, and trans-2-butene. Typically, hydrocarbons other than normal  
17 butene or other C<sub>4-6</sub> normal olefins will be present in the feed stream. These other  
18 hydrocarbons may include, e.g., alkanes, other olefins, aromatics, hydrogen, and inert gases.

19 The feed stream typically may be the effluent from a fluid catalytic cracking unit or a  
20 methyl-tert-butyl ether unit. A fluid catalytic cracking unit effluent typically contains about  
21 40-60 weight percent normal butenes. A methyl-tert-butyl ether unit effluent typically  
22 contains 40-100 weight percent normal butene. The feed stream preferably contains at least  
23 about 40 weight percent normal butene, more preferably at least about 65 weight percent  
24 normal butene. The terms iso-olefin and methyl branched iso-olefin may be used  
25 interchangeably in this specification.

26 The process is carried out under isomerization conditions. The hydrocarbon feed is  
27 contacted in a vapor phase with a catalyst comprising the CIT-5. The process may be  
28 carried out generally at a temperature from about 625°F to about 950°F (329-510°C), for  
29 butenes, preferably from about 700°F to about 900°F (371-482°C), and about 350°F to  
30 about 650°F (177-343°C) for pentenes and hexenes. The pressure ranges from  
31 subatmospheric to about 200 psig, preferably from about 15 psig to about 200 psig, and  
32 more preferably from about 1 psig to about 150 psig.







1 to contain ammonium or a metal cation complement, preferably in the range of from about  
2 0.05 to 5% by weight. The metal cations that may be present include any of the metals of  
3 the Groups I through VIII of the Periodic Table. However, in the case of Group IA metals,  
4 the cation content should in no case be so large as to effectively inactivate the catalyst, nor  
5 should the exchange be such as to eliminate all acidity. There may be other processes  
6 involving treatment of oxygenated substrates where a basic catalyst is desired.

#### 7 Other Uses for CIT-5

8 CIT-5 can also be used as an adsorbent with high selectivities based on molecular  
9 sieve behavior and also based upon preferential hydrocarbon packing within the pores.

10 CIT-5 may also be used for the catalytic reduction of the oxides of nitrogen in a gas  
11 stream. Typically, the gas stream also contains oxygen, often a stoichiometric excess  
12 thereof. Also, the CIT-5 may contain a metal or metal ions within or on it which are capable  
13 of catalyzing the reduction of the nitrogen oxides. Examples of such metals or metal ions  
14 include copper, cobalt and mixtures thereof.

15 One example of such a process for the catalytic reduction of oxides of nitrogen in the  
16 presence of a zeolite is disclosed in U.S. Patent No. 4,297,328, issued October 27, 1981 to  
17 Ritscher et al., which is incorporated by reference herein. There, the catalytic process is the  
18 combustion of carbon monoxide and hydrocarbons and the catalytic reduction of the oxides  
19 of nitrogen contained in a gas stream, such as the exhaust gas from an internal combustion  
20 engine. The zeolite used is metal ion-exchanged, doped or loaded sufficiently so as to  
21 provide an effective amount of catalytic copper metal or copper ions within or on the zeolite.  
22 In addition, the process is conducted in an excess of oxidant, e.g., oxygen.

#### 23 EXAMPLES

24 The following examples demonstrate but do not limit the present invention.

##### 25 Example 1

##### 26 Synthesis of N(16) methylsparteinium hydroxide (MeSPOH)

27 21.1 Grams (50 mmol) of (-) sparteine sulfate pentahydrate (Aldrich) is added to 50 ml of a  
28 3 M NaOH solution. The resulting suspension is stirred until the crystals are completely  
29 dissolved and two phases form. The organic phase is extracted three times with 25 ml  
30 portions of diethyl ether and the combined extracts are dried over solid KOH (85%) and  
31 filtered. The solvent is then evaporated at room temperature under vacuum. The recovered  
32 (-) sparteine is dissolved in 100 ml of acetone containing 28.3 g (1.5 equiv.) of methyl  
33 iodide. The resulting reaction mixture is stirred in the dark for 24 hours. and the yellow

1 solid product which forms is filtered after the addition of 50 ml of diethyl ether. The  
2 recovered solid (15.2 g, 81% yield) is recrystallized twice in 2-propanol by adding ethyl  
3 acetate until turbidity to give 13.7 g (73% yield) of slightly yellow crystals. Analyses:  
4 Calculated for  $C_{16}N_2H_{29}I$ : C, 51.1%; N, 7.4%; H, 7.7%; I, 33.8%. Found: C, 51.0%; N,  
5 7.4%; H, 7.9%; I, 33.7%. The IR spectrum of the product agrees with a previously reported  
6 spectrum for N(16) methylsparteinium iodide.

7 Amberlite IRA-400(Cl) (Aldrich) anion exchange resin, exchanged to the bromide  
8 form, is used to convert the iodide salt prepared as above to the corresponding bromide.  
9 Typically, 7.52 g of N(16) methylsparteinium iodide (20 mmol) is dissolved in 50 ml of  
10 water and exchanged in an ion exchange column containing 100 ml of anion exchange resin  
11 (with 140 mmol of exchange capacity). After washing the column with an additional 200 ml  
12 of distilled water, the aqueous solution obtained is evaporated in a rotavapor until dryness  
13 and recrystallized as described above from 2-propanol-ethyl acetate. Elemental analyses  
14 indicate a yield of 95% for the bromide form. Similarly, the hydroxide form is obtained  
15 using Amberlite IRA-400 (OH) anion exchange resin. After exchange, the aqueous solution  
16 is concentrated to 50 ml. The yield is 92.8% based on titration of the resultant solution and  
17 gives a concentration of 0.371 M of N(16) methylsparteinium hydroxide.

#### 18 Example 2

##### 19 Preparation of Silicate CIT-5

20 0.018 Gram of LiOH anhydrous powder is dissolved in 2.54 g of distilled water. To  
21 the resulting solution is added 2.21 g of N(16) methylsparteinium hydroxide (MeSPA(OH))  
22 solution (18.2 wt%) and the resulting reaction mixture is stirred for 10 minutes.  $SiO_2$   
23 (Ludox HS-30 from E. I. duPont), 1.5 g, is added to the reaction mixture and the mixture is  
24 stirred for two hours. The resulting gel is divided into portions and heated in three quartz  
25 tubes at 175°C for 7 days, 10 days and 11 days at autogenous pressure. The product is  
26 recovered by vacuum filtration and determined by X-ray diffraction (XRD) to be CIT-5 (the  
27 product recovered after 10 days also contains some amorphous material).

28 Typical XRD lines for the as-made (i.e., uncalcined) product of this example is  
29 indicated in Table III below.

1

TABLE III

<u>2 Theta</u>	<u>d</u>	<u>I/I<sub>0</sub> x 100</u>
6.957	12.695	77
7.288	12.119	50
12.810	6.905	4
13.929	6.353	37
17.093	5.183	3
18.963	4.676	100
19.588	4.529	25
20.001	4.436	57
20.499	4.329	40
20.953	4.236	60
21.770	4.079	3
21.931	4.050	8
22.613	3.929	7
23.410	3.797	13
24.218	3.672	6
24.625	3.612	34
25.796	3.451	5
26.097	3.412	7
26.733	3.332	59
27.116	3.286	18
28.224	3.159	28
29.378	3.038	4
29.818	2.994	6
31.374	2.849	11
31.550	2.833	4

32.990	2.713	6
33.980	2.636	5
35.330	2.539	4
35.636	2.517	10
36.417	2.465	7
37.027	2.426	5
37.700	2.384	4
38.731	2.323	4
44.699	2.026	11
49.424	1.843	4

1

Example 3

2

Synthesis of CIT-5 in the Presence of Zinc

3

In a manner similar to that described in Example 2, CIT-5 is made from the following components:

4

5

0.012 g LiOH

6

1.70 g distilled water

7

1.47 g MeSPOAH solution (18.2 wt%)

8

0.043 g  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ 

9

1.0 g  $\text{SiO}_2$  (Ludox HS-30)

10

This produces a gel composition, in terms of mole ratios, as follows:

11

0.1 LiOH : 0.04  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  : 0.2 MeSPOAH :  $\text{SiO}_2$  : 40  $\text{H}_2\text{O}$ 

12

Product is recovered by vacuum filtration after 13 days and 15 days, and determined by XRD to be CIT-5 (the product recovered after 15 days also contains some unknown material).

13

14

15

Typical XRD lines for the as-made product of this example is indicated in Table IV below.

16

1

TABLE IV

<u>2 Theta</u>	<u>d</u>	<u>I/I<sub>0</sub> x 100</u>
6.903	12.794	17
7.268	12.152	43
12.001	7.368	7
12.846	6.886	5
13.841	6.393	9
14.597	6.064	3
16.331	5.423	34
18.930	4.684	61
19.641	4.516	40
19.967	4.443	58
20.432	4.343	40
20.826	4.262	21
21.590	4.113	30
21.963	4.044	18
23.348	3.807	8
24.208	3.674	3
24.548	3.623	20
25.878	3.440	11
26.799	3.324	100
27.146	3.282	23
28.129	3.170	25
29.964	2.990	3
30.209	2.958	2
31.276	2.858	6
31.625	2.827	3

32.913	2.719	4
33.462	2.676	5
33.719	2.656	4
35.569	2.522	20
36.265	2.475	8
37.051	2.424	6
37.848	2.375	5
38.646	2.328	3
44.625	2.029	4
44.828	2.020	6
47.102	1.928	4
49.616	1.836	5

1 After the product is calcined, it has the XRD lines indicated in Table V below.

2

TABLE V

<u>2 Theta</u>	<u>d</u>	<u>I/I<sub>0</sub> x 100</u>
6.913	12.777	39
7.305	12.092	100
12.224	7.235	7
12.921	6.846	13
13.830	6.398	-
13.917	6.358	-
18.995	4.668	41
19.754	4.491	21
20.044	4.426	60
20.503	4.328	47
20.864	4.254	17
21.295	4.169	10



21.645	4.102	28
22.103	4.018	10
22.568	3.937	2
23.409	3.797	6
24.319	3.657	7
24.612	3.614	13
26.016	3.422	7
26.172	3.402	3
26.944	3.306	57
27.282	3.266	16
28.059	3.178	6
28.222	3.160	18
29.910	2.985	3
30.254	2.952	1
31.393	2.847	5
31.778	2.814	1
33.020	2.710	4
33.589	2.666	2
33.876	2.644	0
34.358	2.608	1
35.702	2.513	21
36.289	2.474	3
36.427	2.465	6
37.233	2.413	5
38.024	2.365	3
38.807	2.319	1
43.680	2.070	2

44.596	2.030	1
45.017	2.012	4
45.921	1.975	1
47.293	1.921	3
48.250	1.885	0
48.846	1.863	0
49.869	1.827	3
50.537	1.805	3

1

Example 4

2

Synthesis of Aluminosilicate CIT-5

3

In a manner similar to that described in Example 2, aluminosilicate CIT-5 is made from the following components:

4

5

0.018 g LiOH

6

3.47 g distilled water

7

1.27 g MeSPOH solution (31.0 wt%)

8

0.028 g  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ 

9

1.50 g  $\text{SiO}_2$  (Ludox HS-30)

10

This produces a gel composition, in terms of mole ratios, as follows:

11

 $0.1 \text{ LiOH} : 0.01 \text{ Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O} : 0.2 \text{ MeSPOH} : \text{SiO}_2 : 40 \text{ H}_2\text{O}$ 

12

Product is recovered by vacuum filtration after 7 days and 9 days, and determined by XRD to be CIT-5.

13

14

Typical XRD lines for the as-made product of this example is indicated in Table VI below.

15

1

TABLE VI

<u>2 Theta</u>	<u>d</u>	<u>I/I<sub>0</sub> x 100</u>
6.334	13.942	3
7.000	12.617	100
7.287	12.122	25
12.650	6.992	2
12.825	6.897	3
13.010	6.799	2
13.361	6.621	2
13.972	6.333	58
14.590	6.066	3
18.170	4.878	3
18.323	4.838	3
18.992	4.669	73
19.599	4.526	18
20.032	4.429	41
20.523	4.324	31
20.996	4.228	99
21.800	4.074	3
21.981	4.041	6
23.447	3.791	9
24.251	3.667	5
24.655	3.608	31
25.393	3.505	4
25.802	3.450	3
26.104	3.411	4
26.749	3.330	45

27.148	3.282	13
28.130	3.170	22
28.234	3.158	23
29.836	2.992	3
31.374	2.849	8
33.065	2.707	4
33.481	2.674	4
35.308	2.540	3
35.675	2.515	8
36.492	2.460	7
37.007	2.427	4
37.744	2.382	4
38.796	2.319	3
44.750	2.024	9
47.198	1.924	3
49.639	1.835	2

1 After the product is calcined, it has the XRD lines indicated in Table VII below.

2

TABLE VII

<u>2 Theta</u>	<u>d</u>	<u>I/I<sub>0</sub> x 100</u>
6.922	12.760	100
7.301	12.098	86
12.235	7.228	11
12.920	6.847	6
13.869	6.380	7
17.105	5.180	-
17.161	5.163	1
18.515	4.788	1

18.989	4.670	40
19.730	4.496	11
20.041	4.427	31
20.510	4.327	26
20.876	4.252	26
23.437	3.793	5
24.301	3.660	4
24.613	3.614	18
25.235	3.526	2
26.008	3.423	3
26.147	3.405	4
26.923	3.309	29
27.268	3.268	8
27.947	3.190	4
28.222	3.160	16
29.887	2.987	1
30.223	2.955	1
31.367	2.850	5
31.796	2.812	1
32.232	2.775	1
33.010	2.711	3
33.563	2.668	2
33.849	2.646	1
34.345	2.609	1
35.152	2.551	-
35.690	2.514	7
36.337	2.470	4

37.208	2.415	3
37.591	2.391	1
38.018	2.365	2
38.757	2.322	1
39.350	2.288	-
40.031	2.251	-
40.782	2.211	-
41.103	2.194	-
41.957	2.152	-
42.892	2.107	1
43.694	2.070	1
44.581	2.031	2
44.997	2.013	2
45.937	1.974	1
47.281	1.921	2
48.265	1.884	-
48.863	1.862	-
49.857	1.828	2
50.562	1.804	3

1

Example 5

2

Synthesis of Aluminosilicate CIT-5

3

In a manner similar to that described in Example 2, aluminosilicate CIT-5 is made

4

from the following components:

5

0.18g LiOH

6

3.47g distilled water

7

1.27g MeSPAOH solution (31.0 wt%)

8

0.048g Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O

9

1.5g SiO<sub>2</sub> (Ludox HS-30)

10

This produces a gel composition, in terms of mole ratios, as follows:

11

0.1 LiOH : 0.02 Al(NO<sub>3</sub>)<sub>3</sub> : 0.2 MeSPAOH : SiO<sub>2</sub> : 40 H<sub>2</sub>O

1 Product is recovered after 21 days and determined by XRD to be a mixture of  
2 amorphous material and CIT-5.

### 3 Comparative Example A

#### 4 Attempted Synthesis of Aluminosilicate CIT-5

5 In a manner similar to that described in Example 2, aluminosilicate CIT-5 is made  
6 from the following components:

7 0.18g LiOH

8 3.35g distilled water

9 1.27g MeSPAOH solution (31.0 wt%)

10 0.281g  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$

11 1.5g  $\text{SiO}_2$  (Ludox HS-30)

12 This produces a gel composition, in terms of mole ratios, as follows:

13 0.1 LiOH : 0.1  $\text{Al}(\text{NO}_3)_3$  : 0.2 MeSPAOH :  $\text{SiO}_2$  : 40  $\text{H}_2\text{O}$

14 Product is recovered after 60 days and determined by XRD to be amorphous material.

### 15 Example 6

#### 16 Synthesis of Borosilicate CIT-5

17 In a manner similar to that described in Example 2, borosilicate CIT-5 is made from  
18 the following components:

19 0.18g LiOH

20 3.47g distilled water

21 1.27g MeSPAOH solution (31.0 wt%)

22 0.0046g  $\text{H}_3\text{BO}_3$

23 1.5g  $\text{SiO}_2$  (Ludox HS-30)

24 This produces a gel composition, in terms of mole ratios, as follows:

25 0.1 LiOH : 0.01  $\text{H}_3\text{BO}_3$  : 0.2 MeSPAOH :  $\text{SiO}_2$  : 40  $\text{H}_2\text{O}$

26 Product is recovered after 7 days and determined by XRD to be CIT-5.

### 27 Example 7

#### 28 Synthesis of Gallosilicate CIT-5

29 In a manner similar to that described in Example 2, gallosilicate CIT-5 is made from  
30 the following components:

31 0.18g LiOH

32 3.47g distilled water

33 1.27g MeSPAOH solution (31.0 wt%)

34 0.019g  $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$  ( $x=3.4$ )

35 1.5g  $\text{SiO}_2$  (Ludox HS-30)

36 This produces a gel composition, in terms of mole ratios, as follows:

1                   0.1 LiOH : 0.01 Ga(NO<sub>3</sub>)<sub>3</sub> : 0.2 MeSPA OH : SiO<sub>2</sub> : 40 H<sub>2</sub>O

2 Product is recovered after 7 days and determined by XRD to be CIT-5.

3   Example 8

4   Synthesis of Silicate CIT-5

5           In a manner similar to that described in Example 2, silicate CIT-5 is synthesized in a  
6 Teflon lined autoclave instead of quartz tubes from the following components:

7           0.19g LiOH

8           4.22g distilled water

9           0.86g MeSPA OH solution (49.8 wt%)

10          1.6g SiO<sub>2</sub> (Ludox HS-30)

11 This produces a gel composition, in terms of mole ratios, as follows:

12                                   0.1 LiOH : 0.2 MeSPA OH : SiO<sub>2</sub> : 40 H<sub>2</sub>O

13 Product is recovered after 6 days and determined by XRD to be CIT-5.

14   Example 9

15   Synthesis of Silicate CIT-5 Using Li and Na

16           In a manner similar to that described in Example 8, silicate CIT-5 is synthesized  
17 from the following components:

18          0.14g LiOH

19          0.016g 50 wt% aqueous NaOH solution

20          4.22g distilled water

21          0.86g MeSPA OH solution (49.8 wt%)

22          1.6g SiO<sub>2</sub> (Ludox HS-30)

23 This produces a gel composition, in terms of mole ratios, as follows:

24                                   0.075 LiOH : 0.025 NaOH : 0.2 MeSPA OH : SiO<sub>2</sub> : 40 H<sub>2</sub>O

25 Product is recovered after 5 days and determined by XRD to be CIT-5.

26   Example 10

27   Synthesis of Silicate CIT-5 Using Li and K

28           In a manner similar to that described in Example 8, silicate CIT-5 is synthesized  
29 from the following components:

30          0.14g LiOH

31          0.022g 50 wt% aqueous KOH solution

32          4.22g distilled water

33          0.86g MeSPA OH solution (49.8 wt%)

34          1.6g SiO<sub>2</sub> (Ludox HS-30)

35 This produces a gel composition, in terms of mole ratios, as follows:

36                                   0.075 LiOH : 0.025 KOH : 0.2 MeSPA OH : SiO<sub>2</sub> : 40 H<sub>2</sub>O



1 Product is recovered after 5 days and determined by XRD to be CIT-5 and amorphous  
2 material.

### 3 Example 11

#### 4 Synthesis of Aluminosilicate CIT-5

5 In the Teflon cup for a small Parr reactor is combined 3.4 grams of a 0.66 M solution  
6 of MeSPAOH template with 8.5 grams of water and 0.06 gram of lithium carbonate. 0.90  
7 Gram of 390-HUA Y zeolite (sold by Tosoh) is added as a source of both silicon and  
8 aluminum. The reactor is sealed and heated at 160°C while being tumbled at 43 RPM for a  
9 period of 12 days. Upon cooling the reactor, the solid product is collected by filtration,  
10 washed and dried. The product is determined by XRD to be CIT-5.

11 The CIT-5 product is calcined and ammonium ion exchanged as previously  
12 described.

### 13 Example 12

#### 14 Preparation of Pd CIT-5

15 0.99 Gram of the ammonium exchanged CIT-5 prepared in Example 11 is slurried  
16 into 9 ml of water and 2 ml of a 0.156 N ammonium hydroxide solution. A solution of  
17 palladium tetraamine dinitrate buffered in ammonium hydroxide is then added. The  
18 quantity of palladium is sufficient to provide 0.50 wt% Pd on the CIT-5 if completely ion  
19 exchanged onto the zeolite. The zeolite and solution are allowed to stand for several days at  
20 room temperature, after which the zeolite is filtered and washed. This product is then  
21 calcined at 482°C after a slow ramp to 120°C followed by a 1 degree C/minute increase to  
22 482°C. The zeolite is held at 482°C for three hours.

### 23 Example 13

#### 24 Hydrocracking and Hydroisomerization of n-Hexadecane

#### 25 Using Pd CIT-5

26 0.50 Gram of the Pd CIT-5 prepared in Example 12 is pressed into a tablet at 3000  
27 psi, fractured, meshed to 20-40, and loaded into a stainless steel reactor. The zeolite is dried  
28 in situ and the reactor temperature is brought to 600°F (315°C) and pressurized to 1200 psi  
29 hydrogen flow. A n-hexadecane feed is introduced at 1.00 microliter/minute. At 167 hours  
30 on stream and at 660°F (349°C), the catalyst is achieving 96% conversion. The liquid to gas  
31 ratio of the converted products is 5.3. Iso/normal ratios for the gasoline fractions and  
32 hexadecane are given below.

Carbon No.	Iso/Normal ratio
4	1.95
5	3.19
6	2.89

7	3.52
8	4.20
9	4.69
10	5.82
16	7.87

1

Example 14

2

Adsorption Properties of CIT-5

3

4 A sample of silicate CIT-5 from Example 2 (crystallized for 11 days) is calcined by  
 5 heating it from room temperature to 700°C over a period of three hours and maintaining it at  
 6 700°C for an additional two hours. The calcined sample's adsorption properties are  
 7 determined by a McBain Baker balance. The resulting adsorption properties are -  
 8 cyclohexane: 0.07 ml/g 2,2-dimethylpropane: 0.05 ml/g .

8

Example 15

9

Reactions of m-Xylene Over CIT-5

10

11 CIT-5 with a Si/Al mole ratio of about 200 is pressed into a wafer. The wafer is then  
 12 crushed into small pellets. The pellets are size sorted, and only pellets of the size -35/+70  
 13 are used. 100-150 Milligrams of the catalyst is placed in a downward flow reactor. The  
 14 catalyst is pretreated in a flow of helium at 50 ml/min. with the following temperature  
 15 program:

15

2 hr            2 hr            1.5 hr            3 hr

16

RT -----> 175°C -----> 175°C -----> 350°C -----> 350°C

17

18 The temperature is the decreased to 317°C over 25 minutes and then maintained at  
 19 this temperature for the reaction. The helium flow is reduced to 20 ml/min. and directed  
 20 through a saturator containing m-xylene (Aldrich 99+%) which is kept at 10°C (± 0.5°C).  
 21 The vapor pressure of m-xylene at this temperature is 3.4 torr. The helium/m-xylene stream  
 22 is then passed over the catalyst bed for reaction. Products are analyzed with an on-line gas  
 23 chromatograph. The results are indicated below.

23

Catalyst mass = 116.2 mg

24

Initial conversion = 2.5%

25

Para/Ortho = 0.9

26

Isomerization/Disproportionation = 11

27

28 Only 1,2,4 trimethylbenzene is formed, although this is likely due to the low  
 29 conversion. The 1,3,5 isomer is detected by the gas chromatograph, but the amount of this  
 material is too small to be integrated by the gas chromatograph's integrator.

## 1 WHAT IS CLAIMED IS:

2

3 1. A zeolite comprising an oxide of a tetravalent element or mixture of oxides of  
4 tetravalent elements and, optionally, an oxide of a trivalent element or mixtures of  
5 oxides of trivalent elements and having, after calcination, the X-ray diffraction lines of  
6 Table II.

7

8 2. A zeolite comprising an oxide selected from the group consisting of silicon oxide,  
9 germanium oxide and mixtures thereof and an optional oxide selected from aluminum  
10 oxide, boron oxide, gallium oxide, iron oxide and mixtures thereof, and having, after  
11 calcination, the X-ray diffraction lines of Table II.

12

13 3. A zeolite according to claim 2 wherein the oxides comprise silicon oxide and  
14 aluminum oxide.

15

16 4. A zeolite according to claim 2 wherein the oxides comprise silicon oxide and boron  
17 oxide.

18

19 5. A zeolite according to claim 2 wherein the oxides comprise silicon oxide and gallium  
20 oxide.

21

22 6. A zeolite comprising an oxide of silicon, germanium or mixtures thereof and an oxide  
23 of titanium and having, after calcination, the X-ray diffraction lines of Table II.

24

25 7. A zeolite according to claim 1 wherein said zeolite is predominantly in the hydrogen  
26 form.

27

28 8. A zeolite according to claim 1 wherein said zeolite is substantially free of acidity.

29

30 9. A zeolite having a composition, as synthesized and in the anhydrous state, in terms of  
31 mole ratios as follows:

32 
$$YO_2/W_aO_b > 40$$

1  $M/YO_2 \leq 0.05$

2  $Q/YO_2 \leq 0.05$

3

4 wherein Y is silicon, germanium or a mixture thereof; W is aluminum, boron, gallium,  
5 iron or mixtures thereof; a= 1 or 2, b=2 when a=1 and b=3 when a= 2 ; M is an alkali  
6 metal; and Q comprises a N(16) methylsparteinium cation.

7

8 10. A zeolite according to claim 8 wherein W is aluminum and Y is silicon.

9

10 11 . A zeolite according to claim 8 wherein W is boron and Y is silicon.

11

12 12 . A zeolite according to claim 8 wherein W is gallium and Y is silicon.

13

14 13 . A zeolite having a composition, as synthesized and in the anhydrous state, in terms of  
15 mole ratios as follows:

16  $YO_2/TiO_2 > 40$

17  $M/YO_2 \leq 0.05$

18  $Q/YO_2 \leq 0.05$

19

20 wherein Y is silicon, germanium or a mixture thereof; M is an alkali metal; and Q  
21 comprises a N(16) methylsparteinium cation.

22

23 14. A method of preparing a crystalline material comprising an oxide of a tetravalent  
24 element or mixture of oxides of tetravalent elements and, optionally, an oxide of a  
25 trivalent element or mixtures of oxides of trivalent elements, said method comprising  
26 contacting in admixture under crystallization conditions sources of said oxides, a  
27 source of alkali metal and a templating agent comprising a N(16) methylsparteinium  
28 cation.

29

30 15. The method according to claim 14 wherein the tetravalent element is selected from the  
31 group consisting of silicon, germanium and combinations thereof.

32

- 1 16. The method according to claim 14 wherein the trivalent element is selected from the  
2 group consisting of aluminum, boron, gallium, iron and mixtures thereof.  
3
- 4 17. The method according to claim 14 wherein the tetravalent element is silicon and the  
5 trivalent element is aluminum.  
6
- 7 18. The method according to claim 14 wherein the tetravalent element is silicon and the  
8 trivalent element is boron.  
9
- 10 19. The method according to claim 14 wherein the tetravalent element is silicon and the  
11 trivalent element is gallium.  
12
- 13 20. The method according to claim 14 wherein the tetravalent element is silicon and the  
14 trivalent element is iron.  
15
- 16 21. The method of claim 14 wherein the crystalline material has, after calcination, the  
17 X-ray diffraction lines of Table II.  
18
- 19 22. The method of claim 14 wherein the source of the alkali metal contains no alkali metal  
20 other than lithium.  
21
- 22 23. The method of claim 14 wherein the source of alkali metal contains lithium and  
23 another alkali metal.  
24
- 25 24. The method of claim 14 wherein the admixture further comprises a source of zinc.  
26
- 27 25. A process for converting hydrocarbons comprising contacting a hydrocarbonaceous  
28 feed at hydrocarbon converting conditions with a catalyst comprising a zeolite  
29 comprising an oxide of a tetravalent element or mixture of oxides of tetravalent  
30 elements and an optional oxide of a trivalent element or mixtures of oxides of trivalent  
31 elements and having, after calcination, the X-ray diffraction lines of Table II.  
32

- 1 26. The process of claim 25 wherein the zeolite is predominantly in the hydrogen form.  
2
- 3 27. The process of claim 25 wherein the zeolite is substantially free of acidity.  
4
- 5 28. The process of claim 25 wherein the process is a hydrocracking process comprising  
6 contacting the catalyst with a hydrocarbon feedstock under hydrocracking conditions.  
7
- 8 29. The process of claim 28 wherein the zeolite is predominantly in the hydrogen form.  
9
- 10 30. The process of claim 25 wherein the process is a dewaxing process comprising  
11 contacting the catalyst with a hydrocarbon feedstock under dewaxing conditions.  
12
- 13 31. The process of claim 30 wherein the zeolite is predominantly in the hydrogen form.  
14
- 15 32. The process of claim 25 wherein the process is a process for improving the viscosity  
16 index of a dewaxed product of waxy hydrocarbon feeds comprising contacting the  
17 catalyst with a waxy hydrocarbon feed under isomerization dewaxing conditions.  
18
- 19 33. The process of claim 32 wherein the zeolite is predominantly in the hydrogen form.  
20
- 21 34. The process of claim 25 wherein the process is a process for producing a C<sub>20+</sub> lube oil  
22 from a C<sub>20+</sub> olefin feed comprising isomerizing said olefin feed under isomerization  
23 conditions over the catalyst.  
24
- 25 35. The process of claim 34 wherein the zeolite is predominantly in the hydrogen form.  
26
- 27 36. The process of claim 34 wherein the catalyst further comprises at least one Group VIII  
28 metal.  
29
- 30 37. The process of claim 25 wherein the process is a process for catalytically dewaxing a  
31 hydrocarbon oil feedstock boiling above about 350°F and containing straight chain and  
32 slightly branched chain hydrocarbons comprising contacting said hydrocarbon oil  
33 feedstock in the presence of added hydrogen gas at a hydrogen pressure of about 15-

1           3000 psi under dewaxing conditions with the catalyst.

2

3   38.   The process of claim 37 wherein the zeolite is predominantly in the hydrogen form.

4

5   39.   The process of claim 37 wherein the catalyst further comprises at least one Group VIII  
6       metal.

7

8   40.   The process of claim 37 wherein said catalyst comprises a layered catalyst comprising  
9       a first layer comprising the zeolite and at least one Group VIII metal, and a second  
10      layer comprising an aluminosilicate zeolite which is more shape selective than the  
11      zeolite of said first layer.

12

13   41.   The process of claim 25 wherein the process is a process for preparing a lubricating oil  
14      which comprises:

15

16      hydrocracking in a hydrocracking zone a hydrocarbonaceous feedstock to obtain an  
17      effluent comprising a hydrocracked oil; and

18

19      catalytically dewaxing said effluent comprising hydrocracked oil at a temperature of at  
20      least about 400°F and at a pressure of from about 15 psig to about 3000 psig in the  
21      presence of added hydrogen gas with the catalyst.

22

23   42.   The process of claim 41 wherein the zeolite is predominantly in the hydrogen form.

24

25   43.   The process of claim 41 wherein the catalyst further comprises at least one Group VIII  
26      metal.

27

28   44.   The process of claim 25 wherein the process is a process for isomerization dewaxing a  
29      raffinate comprising contacting said raffinate in the presence of added hydrogen under  
30      isomerization dewaxing conditions with the catalyst.

31

32   45.   The process of claim 44 wherein the zeolite is predominantly in the hydrogen form.

33

- 1 46. The process of claim 44 wherein the catalyst further comprises at least one Group VIII  
2 metal.  
3
- 4 47. The process of claim 44 wherein the raffinate is bright stock.  
5
- 6 48. The process of claim 25 wherein the process is a process for increasing the octane of a  
7 hydrocarbon feedstock to produce a product having an increased aromatics content  
8 comprising contacting a hydrocarbonaceous feedstock which comprises normal and  
9 slightly branched hydrocarbons having a boiling range above about 40°C and less than  
10 about 200°C under aromatic conversion conditions with the catalyst.  
11
- 12 49. The process of claim 48 wherein the zeolite is substantially free of acid.  
13
- 14 50. The process of claim 48 wherein the zeolite contains a Group VIII metal component.  
15
- 16 51. The process of claim 25 wherein the process is a catalytic cracking process comprising  
17 contacting a hydrocarbon feedstock in a reaction zone under catalytic cracking  
18 conditions in the absence of added hydrogen with the catalyst.  
19
- 20 52. The process of claim 51 wherein the zeolite is predominantly in the hydrogen form.  
21
- 22 53. The process of claim 51 wherein the catalyst additionally comprises a large pore  
23 crystalline cracking component.  
24
- 25 54. The process of claim 25 wherein the process is an isomerization process for  
26 isomerizing C<sub>4</sub> to C<sub>7</sub> hydrocarbons, comprising contacting a feed having normal and  
27 slightly branched C<sub>4</sub> to C<sub>7</sub> hydrocarbons under isomerizing conditions with the  
28 catalyst.  
29
- 30 55. The process of claim 54 wherein the zeolite is predominantly in the hydrogen form.  
31
- 32 56. The process of claim 54 wherein the zeolite has been impregnated with at least one  
33 Group VIII metal.



1

2 57. The process of claim 54 wherein the catalyst has been calcined in a steam/air mixture  
3 at an elevated temperature after impregnation of the Group VIII metal.

4

5 58. The process of claim 56 wherein the Group VIII metal is platinum.

6

7 59. The process of claim 25 wherein the process is a process for alkylating an aromatic  
8 hydrocarbon which comprises contacting under alkylation conditions at least a molar  
9 excess of an aromatic hydrocarbon with a C<sub>2</sub> to C<sub>20</sub> olefin under at least partial liquid  
10 phase conditions and in the presence of the catalyst.

11

12 60. The process of claim 59 wherein the zeolite is predominantly in the hydrogen form.

13

14 61. The process of claim 59 wherein the olefin is a C<sub>2</sub> to C<sub>4</sub> olefin.

15

16 62. The process of claim 61 wherein the aromatic hydrocarbon and olefin are present in a  
17 molar ratio of about 4:1 to about 20:1, respectively.

18

19 63. The process of claim 61 wherein the aromatic hydrocarbon is selected from the group  
20 consisting of benzene, toluene, ethylbenzene, xylene, or mixtures thereof.

21

22 64. The process of claim 25 wherein the process is a process for transalkylating an  
23 aromatic hydrocarbon which comprises contacting under transalkylating conditions an  
24 aromatic hydrocarbon with a polyalkyl aromatic hydrocarbon under at least partial  
25 liquid phase conditions and in the presence of the catalyst.

26

27 65. The process of claim 64 wherein the zeolite is predominantly in the hydrogen form.

28

29 66. The process of claim 64 wherein the aromatic hydrocarbon and the polyalkyl aromatic  
30 hydrocarbon are present in a molar ratio of from about 1:1 to about 25:1, respectively.

31

32 67. The process of claim 64 wherein the aromatic hydrocarbon is selected from the group  
33 consisting of benzene, toluene, ethylbenzene, xylene, or mixtures thereof.

34

35 68. The process of claim 64 wherein the polyalkyl aromatic hydrocarbon is a  
36 dialkylbenzene.

1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32

69. The process of claim 25 wherein the process is a process to convert paraffins to aromatics which comprises contacting paraffins under conditions which cause paraffins to convert to aromatics with a catalyst comprising the zeolite and gallium, zinc, or a compound of gallium or zinc.

70. The process of claim 25 wherein the process is a process for isomerizing olefins comprising contacting said olefin under conditions which cause isomerization of the olefin with the catalyst.

71. The process of claim 25 wherein the process is a process for isomerizing an isomerization feed comprising an aromatic C<sub>8</sub> stream of xylene isomers or mixtures of xylene isomers and ethylbenzene, wherein a more nearly equilibrium ratio of ortho-, meta and para-xylenes is obtained, said process comprising contacting said feed under isomerization conditions with the catalyst.

72. The process of claim 25 wherein the process is a process for oligomerizing olefins comprising contacting an olefin feed under oligomerization conditions with the catalyst.

73. A process for converting lower alcohols and other oxygenated hydrocarbons comprising contacting said lower alcohol or other oxygenated hydrocarbon under conditions to produce liquid products with a catalyst comprising a zeolite comprising an oxide of a tetravalent element or mixture of oxides of tetravalent elements and, optionally, an oxide of a trivalent element or mixtures of oxides of trivalent elements and having, after calcination, the X-ray diffraction lines of Table II.

74. In a process for the reduction of oxides of nitrogen contained in a gas stream in the presence of oxygen wherein said process comprises contacting the gas stream with a zeolite, the improvement comprising using as the zeolite a zeolite comprising an oxide of a tetravalent element or mixture of oxides of tetravalent elements and, optionally, an oxide of a trivalent element or mixtures of oxides of trivalent elements and having,

- 1           after calcination, the X-ray diffraction lines of Table II.
- 2
- 3    75.   The process of claim 74 wherein said zeolite contains a metal or metal ions capable of
- 4           catalyzing the reduction of the oxides of nitrogen.
- 5
- 6    76.   The process of claim 75 wherein the metal is copper, cobalt or mixtures thereof.
- 7
- 8    77.   The process of claim 75 wherein the gas stream is the exhaust stream of an internal
- 9           combustion engine.

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 98/16401

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC 6	C01B39/48	C01B39/08	C01B39/12	C01B37/02	B01J29/70
	B01J29/86	B01J29/87	C10G45/64	C10G65/04	C10G65/12
	C10G35/095	C07C2/66	C07C6/12	C07C5/41	C07C5/22

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 C01B C10G

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.
P, X	PAUL WAGNER ET AL.: "CIT-5: a high-silica zeolite with 14-ring pores" CHEMICAL COMMUNICATIONS., no. 22, 21 November 1997, pages 2179-2180, XP002086050 SOCIETY OF CHEMISTRY GB see the whole document ---	1-3, 7-10, 13-17, 21, 22
A	US 5 271 922 A (NAKAGAWA YUMI) 21 December 1993 see the whole document ---	1-24
A	US 4 936 977 A (ZONES STACEY I ET AL) 26 June 1990 see the whole document ---	1-5, 7-12, 25
	-/--	

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
- "E" earlier document but published on or after the international filing date
- "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)
- "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

3 December 1998

Date of mailing of the international search report

28/12/1998

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

Rigondaud, B

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 98/16401

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> IPC 6 C07C5/27 C07C2/12 C10G50/00 C10G3/00 B01D53/047				
According to International Patent Classification (IPC) or to both national classification and IPC				
<b>B. FIELDS SEARCHED</b>				
Minimum documentation searched (classification system followed by classification symbols)				
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)				
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>				
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.		
A	WO 95 22507 A (CHEVRON USA INC) 24 August 1995 see claims 1-47 see page 21 - page 35 ---	1,25-73		
A	US 5 580 540 A (NAKAGAWA YUMI) 3 December 1996 see column 10, line 5 - column 18, line 31 -----	1,25-77		
<input type="checkbox"/> Further documents are listed in the continuation of box C.				
<input checked="" type="checkbox"/> Patent family members are listed in annex.				
° Special categories of cited documents :				
<table style="width: 100%; border: none;"> <tr> <td style="width: 50%; border: none; vertical-align: top;">                     "A" document defining the general state of the art which is not considered to be of particular relevance                      "E" earlier document but published on or after the international filing date                      "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)                      "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                 </td> <td style="width: 50%; border: none; vertical-align: top;">                     "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.                      "&amp;" document member of the same patent family                 </td> </tr> </table>			"A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "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) "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
"A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "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) "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  <p style="text-align: center; font-weight: bold;">3 December 1998</p>	Date of mailing of the international search report			
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  <p style="text-align: center; font-weight: bold;">Rigondaud, B</p>			

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 98/16401

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5271922 A	21-12-1993	NONE	
<hr style="border-top: 1px dashed black;"/>			
US 4936977 A	26-06-1990	AU 592617 B	18-01-1990
		AU 6806087 A	30-07-1987
		CA 1279058 A	15-01-1991
		EP 0231019 A	05-08-1987
		IN 169668 A	30-11-1991
		JP 1825705 C	28-02-1994
		JP 62191418 A	21-08-1987
		US 4834958 A	30-05-1989
<hr style="border-top: 1px dashed black;"/>			
WO 9522507 A	24-08-1995	AU 1699495 A	04-09-1995
		EP 0746529 A	11-12-1996
		US 5653956 A	05-08-1997
		US 5685973 A	11-11-1997
		US 5770175 A	23-06-1998
<hr style="border-top: 1px dashed black;"/>			
US 5580540 A	03-12-1996	AU 1020297 A	27-06-1997
		CA 2238059 A	12-06-1997
		EP 0863844 A	16-09-1998
		WO 9720769 A	12-06-1997
		US 5683572 A	04-11-1997
<hr style="border-top: 1px dashed black;"/>			