

PRODUCTION OF HYDROCRACKED LUBRICANTS

This invention relates to the production of high viscosity index lubricants by hydrocracking mineral oil feedstocks, especially distillate stocks.

5 Mineral oil based lubricants are conventionally produced by a separative sequence carried out in the petroleum refinery which comprises fractionation of a paraffinic crude oil under atmospheric pressure followed by fractionation under vacuum to produce
10 distillate fractions (neutral oils) and a residual fraction which, after deasphalting and severe solvent treatment may also be used as a lubricant basestock usually referred to as bright stock. Neutral oils, after solvent extraction to remove low viscosity index
15 (V.I.) components are conventionally subjected to dewaxing, either by solvent or catalytic dewaxing processes, to the desired pour point, after which the dewaxed lubestock may be hydrofinished to improve stability and remove color bodies. This conventional
20 technique relies upon the selection and use of crude stocks, usually of a paraffinic character, which produce the desired lube fractions of the desired qualities in adequate amounts. The range of permissible crude sources may, however, be extended by
25 the lube hydrocracking process which is capable of utilizing crude stocks of marginal or poor quality, usually with a higher aromatic content than the best paraffinic crudes. The lube hydrocracking process, which is well established in the petroleum refining
30 industry, generally comprises an initial hydrocracking step carried out under high pressure in the presence of a bifunctional catalyst which effects partial saturation and ring opening of the aromatic components

which are present in the feed. The hydrocracked product is then subjected to dewaxing in order to reach the target pour point since the products from the initial hydrocracking step which are paraffinic in character include components with a relatively high pour point which need to be removed in the dewaxing step.

In theory, as well as in practice, lubricants should be highly paraffinic in nature since paraffins possess the desirable combination of low viscosity and high viscosity index. Normal paraffins and slightly branched paraffins e.g. n-methyl paraffins, are waxy materials which confer an unacceptably high pour point on the lube stock and are therefore removed during the dewaxing operations in the conventional refining process described above. It is, however, possible to process waxy feeds in order to retain many of the benefits of their paraffinic character while overcoming the undesirable pour point characteristic. A severe hydrotreating process for manufacturing lube oils of high viscosity index is disclosed in Developments in Lubrication PD 19(2), 221-228, S. Bull et al, and in this process, waxy feeds such as waxy distillates, deasphalted oils and slack waxes are subjected to a two-stage hydroprocessing operation in which an initial hydrotreating unit processes the feeds in blocked operation with the first stage operating under higher temperature conditions to effect selective removal of the undesirable aromatic compounds by hydrocracking and hydrogenation. The second stage operates under relatively milder conditions of reduced temperature at which hydrogenation predominates, to adjust the total aromatic content and influence the distribution of aromatic types in the final product. The viscosity and

flash point of the base oil are then controlled by topping in a subsequent redistillation step after which the pour point of the final base oil is controlled by dewaxing in a solvent dewaxing (MEK-toluene) unit. The slack waxes removed from the dewaxer may be reprocessed to produce a base oil of high viscosity index.

Processes of this type, employing a waxy feed which is subjected to hydrocracking over an amorphous bifunctional catalyst such as nickel-tungsten on alumina or silica-alumina are disclosed, for example, in British Patents Nos. 1,429,494, 1,429,291 and 1,493,620 and U.S. Patents Nos. 3,830,273, 3,776,839, 3,794,580, and 3,682,813.

In processes of this kind, the hydrocracking catalyst is typically a bifunctional catalyst containing a metal hydrogenation component on an amorphous acidic support. The metal component is usually a combination of base metals, with one metal selected from the iron group (Group VIII) and one metal from Group VIB of the Periodic Table, for example, nickel in combination with molybdenum or tungsten. The activity of the catalyst may be increased by the use of fluorine, either by incorporation into the catalyst during its preparation in the form of a suitable fluorine compound or by in situ fluoriding during the operation of the process, as disclosed in GB 1,390,359.

Although the lube hydrocracking process using an amorphous catalyst for the treatment of the waxy feeds has shown itself to be capable of producing high V.I. lubricants, it is not without its limitations. In particular, there are environmental and metallurgical (corrosion) concerns associated with the use of fluorine and other promoters used with these catalysts; the unfluorided catalysts do not have sufficient cracking

activity to be commercially viable for these applications. While the amorphous catalysts are effective for the saturation of the aromatics under the high pressure conditions which are typically used in lube hydrocracking (2,000 psig) their activity and selectivity for isomerization of the paraffinic components is not as high as might be desired; the relatively straight chain paraffins are not, therefore, isomerized to the less waxy isoparaffins of relatively high viscosity index but with low pour point properties, to the extent required to fully meet product pour point specifications.

Crystalline materials, especially the large pore size zeolites such as zeolites X and Y, have been found to be useful for a number of hydrocracking applications since they have the advantage, as compared to the amorphous materials, of possessing a greater degree of activity, which enables the hydrocracking to be carried out at lower temperatures at which the accompanying hydrogenation reactions are thermodynamically favored. In addition, the crystalline catalysts tend to be more stable in operation than the amorphous materials such as alumina. The crystalline materials may, however, not be suitable for all applications since even the largest pore sizes in these materials, typically 7.4 Å in the X and Y zeolites, are too small to permit access by various bulky species in the feed, such as the high molecular weight species in lube feeds. As a result, the crystalline zeolite catalysts, while very active for boiling range conversion, are not as selective in terms of high lube yield and yield selectivity. For these reasons, lube hydrocracking processes have not used the crystalline catalysts but, instead, have remained with the promoted amorphous catalysts.

One approach to the production of lubes from unconventional refinery streams using crystalline catalysts is disclosed in U.S. Patent Nos. 4,919,788 and 4,975,177. In this process, a zeolite beta catalyst is used to isomerize the high molecular weight paraffins contained in the back end of the feed to less waxy materials while minimizing cracking of these components to materials boiling outside the lube range. The waxy paraffins in the front end of the feed are removed in a subsequent dewaxing step, either solvent or catalytic, in order to achieve the target pour point. While this zeolite-catalyzed process has shown itself to be highly effective for dealing with waxy, highly paraffinic feeds, the high isomerization selectivity of the zeolite beta catalysts, coupled with its lesser capability to remove low quality aromatic components, has tended to limit the application of the process to feeds which contain relatively low quantities of aromatics.

In spite of their shortcomings, therefore, the amorphous catalysts have remained the catalysts of choice for lube hydrocracking even though from some points of view the crystalline zeolite catalysts would appear to offer advantages, at least, in some respects. Clearly, however, it would be desirable to develop a process for producing lubes from unconventional sources or from refinery streams of marginal or unacceptable quality. It would also be desirable to develop a lube hydrocracking process using a catalyst possessing the activity and stability of the crystalline materials coupled with the ability of the amorphous materials to handle the bulky molecular species associated with lube range feeds and products.

5 It has now been found that mesoporous siliceous materials may be used as the basis for hydrocracking catalysts of excellent properties. The catalysts based on these novel materials are capable of functioning as highly effective lube hydrocracking (LHDC) catalysts and of producing high VI lubricating oils without the use of promoters such as fluorine.

10 These mesoporous siliceous materials have a novel and unique pore geometry and, in a preferred form described below, are characterized by a substantially uniform hexagonal honeycomb microstructure with uniform pores having a cell diameter greater than 13 Å and typically in the range of 20 to 100 Å. Most prominent among these materials is a new metallosilicate
15 identified as MCM-41 which is usually synthesized with Brønsted acid sites by incorporating a tetrahedrally coordinated trivalent element such as Al, Ga, B, or Fe within the silicate framework. Aluminosilicate materials of this type possess good thermal and
20 chemical stability and may be used as the basis for LHDC catalysts which exhibit the correct balance of hydrocracking activity and aromatic saturation selectivity to produce conventional VI lubricating oils (i.e. 75-100 VI) in higher lube yields compared to
25 unpromoted USY and amorphous catalysts. Furthermore, the present catalysts exhibit improved conversion activity compared to conventional amorphous fluorided catalysts with only a slight penalty in lube yield/VI selectivity. Thus, the present process involves lube
30 hydrocracking (LHDC) heavy distillates utilizing unpromoted (without the addition of fluorine) ultra large pore size molecular sieve catalysts to produce high VI lubricating oils.

The unpromoted LHDC catalysts based on the mesoporous crystalline materials, as described below, for example, NiW/MCM-41, have the correct balance of cracking activity and lube yield/VI selectivity to make them very attractive alternatives to current fluorided NiW/alumina catalysts. The present mesoporous catalysts result in higher lube yield/VI selectivity compared to USY and unfluorided amorphous catalysts and they also have very good activity compared to the amorphous catalysts in the same application.

Figure 1 of the accompanying drawings is a graph showing the relationship between lube yield and product VI for lube products produced by hydrocracking a distillate feed with various catalysts, as described below in the Examples. Figures 2-5 are graphs which illustrate the relationship between process and product characteristics for lube products produced by the hydrocracking and hydroisomerization of a wax feed with various catalysts.

The feedstock for the present process may generally be characterized as a lube fraction prepared from a crude stock of suitable characteristics. In the direct production of lube stocks from crude, the crude will be subjected to various conventional processes such as distillation in atmospheric and vacuum towers in order to obtain a fraction of the requisite boiling point which may be used as the feed in the present process; in conventional lube processing, the distillate is subjected to removal of the aromatics using a suitable solvent, using a solvent such as phenol, furfural, NMP or another conventional type of solvent for this purpose. If the lube stock is a residual lube stock, removal of asphaltenes and some aromatics will generally be effected in a deasphalting

operation, e.g. a propane deasphalting (PDA) step, as is conventional for the production of residual lube stocks such as bright stock. The deasphalted oil (DAO) from the deasphalting operation is a suitable feed for the present process. After deasphalting, a solvent extraction may be used to reduce the residual aromatics concentration. At this point, the lube stock will typically have a boiling point above 345°C (650°F) except for the lightest lubes but the lube stocks which may be used are generally characterized in terms of their viscosity rather than their boiling ranges since this is a more important characteristic for a lubricant. Generally, if the lube base stock is a distillate base stock, i.e. a neutral stock, it will have a viscosity in the range of 100 to 750 SUS (20 to 160 mm²/s) at 40°C (99°F) and in the case of a bright stock, the viscosity will generally be in the range of 1000 to 3000 SUS (210 to 600 mm²/s) at 99°C (210°F). The light neutral stocks are generally characterized by their Saybolt viscosity at 40°C, e.g. as a 100 second neutral which has a viscosity of 100 SUS at 40°C (20 mm²/s) a 300 second neutral has a viscosity of 300 SUS at 40°C (65 mm²/s) and a heavy neutral will typically have a viscosity of up to 750 SUS (160 mm²/s). However, these specific viscosities and viscosity ranges are not critical but will depend upon the appropriate uses for which the lubricants are to be put. They are quoted here as exemplary of the types of lube stocks to which the present process may be applied.

The distillate (neutral) base stocks may generally be characterized as paraffinic in character, although they also contain naphthenes and aromatics and because of their paraffinic character, they are generally of

fairly low viscosity and high viscosity index. The distillates may be of high sulfur and nitrogen content, for example, containing from 800 to 1000 ppmw nitrogen and up to 1 to 3 wt.% sulfur. The wax content of the distillate is typically from 10 to 15 wt.% but, as discussed below, high wax contents are not undesirable since waxy feeds are capable of producing hydrocracked products with extremely high VI values. The residual stocks obtained from DAO will be more aromatic in character and for this reason will generally have higher viscosities and lower viscosity indices. In general, the aromatic content of the stock will be in the range of 10 to 70 wt.%, usually 15 to 60 wt.% with the residual stocks having the relatively higher aromatic contents, typically 20 to 70 wt.%, more commonly 30 to 60 wt.% and the distillate stocks having lower aromatic contents, for instance, 10 to 30 wt.%. Nitrogen and sulfur contents will characteristically be higher than with the distillate stocks. Fractions in the gas oil boiling range (315°C+ (600°F+)) with an end point usually below 565°C (1050°F) are a convenient feed because they can generally be treated by the present process to produce high quality lubes.

In addition to lube stocks produced directly from crudes, as described above, the hydrocracking process may be adapted to the use of other petroleum refinery streams of suitable characteristics and refining them so as to produce lubricants of extremely good properties. In particular, it is capable of producing lubricants from a feed comprising a petroleum wax containing at least 30, and preferably at least 50, wt.% wax, as determined by ASTM test D-3235. In these feeds of mineral oil origin, the waxes are mostly paraffins of high pour point, comprising straight chain

and slightly branched chain paraffins such as methylparaffins. Product quality and yield are directly related to the feed wax content in that a high wax level in the feed can be converted into a high level of high VI, low pour, iso-paraffins in the product while maintaining a high lube (650°F+) yield. Lower wax levels in the feed imply a higher oil (non-wax) content and because the oil contains components of lower lube quality, mostly cyclic materials such as aromatics and polynaphthenes, this translates into a lower product quality unless these low quality components are removed, implying a lower yield. For these reasons, the use of the high wax content (50 percent minimum wax) feeds is preferred but not indispensable at the expense of product quality or yield.

Petroleum waxes, that is, waxes of paraffinic character are derived from the refining of petroleum and other liquids by physical separation from a wax-containing refinery stream, usually by chilling the stream to a temperature at which the wax separates, usually by solvent dewaxing, e.g., MEK/toluene dewaxing or by means of an autorefrigerant process such as propane dewaxing. These waxes have high initial boiling points above 345°C (650°F) which render them extremely useful for processing into lubricants which also require an initial boiling point of at least 345°C (650°F). The presence of lower boiling components is not to be excluded since they will be removed together with products of similar boiling range produced during the processing during the separation steps which follow the characteristic processing steps. Since these components will, however, load up the process units they are preferably excluded by suitable choice of feed

cut point. The end point of wax feeds derived from the solvent dewaxing of neutral oils, i.e. distillate fractions produced by the vacuum distillation of long or atmospheric resids, will usually be not more than 595°C (1100°F) so that they may normally be classified as distillate rather than residual streams but high boiling wax feeds such as petrolatum waxes, i.e. the waxes separated from bright stock dewaxing, which may typically have an end point of up to 705°C (1300°F), may also be employed.

The wax content of the feed is high, at least 30, more usually at least 50 wt.% for lube products with a VI of at least 135 or higher. Normally, for the highest quality products, feeds with a wax content of 60 to 80 wt.% are preferred. The balance in each case is from occluded oil comprising iso-paraffins, aromatics and naphthenics. The non-wax content of aromatics, polynaphthenes and highly branched naphthenes will normally not exceed 40 wt.% of the wax and preferably will not exceed 25 to 30 wt.%. These waxy, highly paraffinic wax stocks usually have low viscosities because of their relatively low content of aromatics and naphthenes although the high content of waxy paraffins gives them melting points and pour points which render them unacceptable as lubricants without further processing.

Feeds of this type will normally be slack waxes, that is, the waxy product obtained directly from a solvent dewaxing process, e.g. an MEK or propane dewaxing process. The slack wax, which is a solid to semi-solid product, comprising mostly highly waxy paraffins (mostly n- and mono-methyl paraffins) together with occluded oil, may be fed directly to the first step of the present processing sequence as

described below without the requirement for any initial preparation, for example, by hydrotreating.

The compositions of some typical waxes are given in Table 1 below.

5

Table 1

Wax Composition - Arab Light Crude

	A	B	C	D
Paraffins, wt.%	94.2	81.8	70.5	51.4
Mono-naphthenes, wt.%	2.6	11.0	6.3	16.5
10 Poly-naphthenes, wt.%	2.2	3.2	7.9	9.9
Aromatics, wt.%	1.0	4.0	15.3	22.2

15

A typical slack wax feed has the composition shown in Table 2 below. This slack wax is obtained from the solvent (MEK) dewaxing of a 300 SUS (65 cST) neutral oil obtained from an Arab Light crude.

Table 2
Slack Wax Properties

	API	39
	Hydrogen, wt.%	15.14
5	Sulfur, wt.%	0.18
	Nitrogen, ppmw	11
	Melting point, °C (°F)	57 (135)
	KV at 100°C, cSt	5.168
	PNA, wt.%:	
10	Paraffins	70.3
	Naphthenes	13.6
	Aromatics	16.3
	Simulated Distillation:	
	<u>°</u>	<u>°C</u> (<u>°F</u>)
15	5	375 (710)
	10	413 (775)
	30	440 (825)
	50	460 (860)
	70	482 (900)
20	90	500 (932)
	95	507 (945)

Another slack wax suitable for use in the present process has the properties set out in Table 3 below. This wax is prepared by the solvent dewaxing of a 450 SUS (100 cS) neutral raffinate:

25

Table 3
Slack Wax Properties

	Boiling range, °F(°C)	708-1053 (375-567)
	API 35.2	
5	Nitrogen, basic, ppmw	23
	Nitrogen, total, ppmw	28
	Sulfur, wt.%	0.115
	Hydrogen, wt.%	14.04
	Pour point, °F (°C)	120 (50)
10	KV (100°C)	7.025
	KV (300°F, 150°C)	3.227
	Oil (D 3235)	35
	Molecular wt.	539
	P/N/A:	
15	Paraffins	-
	Naphthenes	-
	Aromatics	10

Slack waxes will normally contain from 30 to 80 ppmw of nitrogen with an oil content of 20 to 40 wt.%. They may be processed to give dewaxed lube products with a VI of at least 135, often from 140 to 145 or even higher.

A typical highly paraffinic fraction which may be treated by the present process to form a high quality, high VI lube is a 345°-540°C (650°-1000°F) Minas gas oil having the properties set out in Table 4 below.

Table 4

Minas Gas Oil

	Normal boiling range, °C (°F)	345°-540° (650°-1000°)
	API Gravity	33.0
5	Hydrogen, wt.%	13.6
	Sulfur, wt.%	0.07
	Nitrogen, ppmw	320
	Basic Nitrogen, ppmw	160
	CCR	0.04
10	Composition, wt.%	
	Paraffins	60
	Naphthenes	23
	Aromatics	17
	Bromine No.	0.8
15	KV, 100°C, mm ² /s	4.18
	Pour Point, °C (°F)	46 (115)
	95% TBP, °C (°F)	510 (950)

The feed may be hydrotreated before the hydrocracking/hydroisomerization step in order to remove heteroatom containing impurities and to hydrogenate at least some of the aromatics which may be present to form naphthenes. For de-oiled waxes, however, this pre-treatment will not normally be necessary since the removal of the occluded oil will remove many of the deleterious materials in the foots oil. Inorganic nitrogen and sulfur formed during the hydrotreating may be removed by a conventional separation prior to the catalytic dewaxing.

Conventional hydrotreating catalysts and conditions are suitably used. Catalysts typically comprise a base metal hydrogenation component such as nickel, tungsten, cobalt, nickel-tungsten, nickel-molybdenum or cobalt-molybdenum, on an inorganic oxide support of low acidity such as silica, alumina or silica-alumina,

generally of a large pore, amorphous character. Typical hydrotreating conditions use moderate temperatures and pressures, e.g. 290°-425°C (550°-800°F), typically 345°-400°C (650°-750°F), up to 20,000 kPa (3000 psig), typically 4250-14000 kPa (600-2000 psig) hydrogen pressure, space velocity of 0.3-2.0, typically 1 LHSV, with hydrogen circulation rates typically 600-1800 n.l.l.⁻¹ (3,370 to 10,100 SCF/Bbl) usually 1,300 n.l.l.⁻¹ (7,300 SCF/Bbl). The severity of the hydrotreating step should be selected according to the characteristics of the feed; the objectives being to reduce residual aromatic content by saturation to form naphthenes so as to make initial improvements in lube quality by removal of aromatics and formation of naphthenes, as well as to remove heteroatom-containing impurities, especially sulfur, in order to improve the color and oxidative stability of the final lube products. The hydrotreating severity will therefore usually be greater with residual lube stocks such as bright stock because of their relatively high aromatic and sulfur contents.

The feed to the hydrocracking reactor is processed in the presence of hydrogen in the presence of the ultra-large pore size catalyst.

The feedstock is heated to an elevated temperature and is then passed over the hydrocracking/hydroisomerization catalysts in the presence of hydrogen. The objective of the process is primarily to saturate aromatics and to carry out hydrocracking of the oil and waxes, with isomerization of the waxes to lower pour point iso-paraffins. The large pore structure of the present crystalline catalysts is well adapted to these ends because it permits ready access to the metal sites where hydrogenation takes place and

also permits high metals loading on the support which favors the hydrogenation reactions. Because the thermodynamics of hydrocracking become unfavorable at temperatures above 450°C (850°F) temperatures above this value will not normally be used. The exact temperature chosen will depend on the activity of the catalyst selected and on the feed and product qualities which, in turn, set the appropriate conversion. Thus, the temperature should be selected empirically after consideration of the relevant factors. The hydrotreating and hydrocracking reactions are net exothermic and for this reason, the feedstock need not be heated to the temperature desired in the catalyst bed which is normally in the range 290°, usually 360°C, to 440°C (550°, usually, 675° to 825°F). In many cases, temperatures from 700° to 750°F (370° to 400°C) will be suitable for most wax feeds. At the beginning of the process cycle, the temperature employed will be at the lower end of this range but as the catalyst ages, the temperature may be increased in order to maintain the desired degree of activity.

The feedstock is passed over the catalysts in the presence of hydrogen. The space velocity of the heavy oil is usually in the range 0.1 to 10 LHSV, preferably 0.2 to 2.0 LHSV and the hydrogen circulation rate from 250 to 1,500 n.l.l.⁻¹. (1400 to 8,427 SCF/bbl) and more usually from 300 to 800 (1685 to 4500 SCF/bbl). Wax feeds can be operated at a higher space velocity, typically 1 to 2 LHSV and a hydrogen circulation rate of from 250 to 1500 n.l.l.⁻¹ (1400 to 8427 SCF/bbl) and more usually from 300 to 900 n.l.l.⁻¹ (1685 to 5050 SCF/bbl). For distillates, the preferred range is 0.5 to 0.75. Hydrogen partial pressure is usually at least 75 percent of the total system pressure with reactor

inlet pressures normally being in the range of 3000 to 30,000 kPa (420 to 4,335 psig). High pressure operation is normally preferred in order to saturate aromatics and to facilitate the formation of the more desirable naphthenes and paraffins. Pressures will therefore usually be at least 8,400 kPa (1200 psig) and often above 15,000 kPa (2160 psig), most often in the range of 10,000 to 18,000 kPa (1435 to 2600 psig). Conversion to products boiling outside the lube range, typically to 345°C- (about 650°F-) products, is normally from 5 to 70 volume percent, more usually from 10 to 40 volume percent, depending on the feed and the target VI for the product. With distillate feeds, the boiling range conversion will typically be in the range of 15 to 40 percent for products with a target VI (dewaxed product) of 120 with lower boiling range conversions in the range of 15 to 25 percent appropriate for products in the 95 - 100 VI range. For slack wax feeds, the boiling range conversion will typically be in the range of 25 to 35 percent for dewaxed products with a target VI of 135 or higher. Product VI will therefore usually be from 95 to 140.

For wax feeds, pressures will usually be at least 1,000 psig (7,000 kPa Abs) up to 3,000 psig (20,000 kPa), usually from 1435 psig (10,000 kPa) to 2600 psig (18,000 kPa abs). Conversion to products boiling outside the lube range, typically to 345°C- (650°F-) products, is normally at least 15 percent, and usually from 25 to 60, usually 25 to 35 percent, for dewaxed products with a target VI of 135 or higher. Boiling point conversion (for 650°F-) is defined as:

650°F- conversion =

$$\frac{650^{\circ}\text{F}+ \text{ in Feed} - 650^{\circ}\text{F}+ \text{ in Product}}{650^{\circ}\text{F}+ \text{ in Feed}}$$

The wax conversion will be from 10 to 90 percent but is preferably in the range of 50 to 70 wt.% for products with a VI of at least 135 and usually at least 140. Wax conversion is defined as:

$$\begin{array}{lcl} 5 & \text{Wax Conversion} = & \frac{\text{Wt.\% Unconverted Wax}}{\text{Wt.\% Wax in Feed - after Solvent Dewaxing}} \\ & & \text{Wt.\% Wax in Feed} \end{array}$$

10 The hydrocracked/hydroisomerized (HDC/HDI) product may be dewaxed if necessary to target pour point after the HDC/HDI step. A notable feature of the present process is that the extent of dewaxing required is relatively small. Typically, the loss during the final dewaxing step will be no more than 15 to 20 wt.% of the dewaxer feed and may be lower. Either catalytic
15 dewaxing or solvent dewaxing may be used at this point and if a solvent dewaxer is used, the removed wax may be recycled to the first or second stages of the process for further treatment. Since the wax removed in a solvent dewaxer is highly paraffinic, it may be
20 recycled directly to the second stage if this is feasible, for example, in the embodiment where the second stage is operated at a relatively low pressure.

The preferred catalytic dewaxing processes utilize an intermediate pore size zeolite such as ZSM-5, but
25 the most preferred dewaxing catalysts are based on the highly constrained intermediate pore size zeolites such as ZSM-22, ZSM-23 or ZSM-35, since these zeolites have been found to provide highly selective dewaxing, giving dewaxed products of low pour point and high VI.
30 Dewaxing processes using these zeolites are described in U.S. Patent Nos. 4,222,855. The zeolites whose use is preferred here may be characterized in the same way as described in U.S. 4,222,855, i.e. as zeolites having

pore openings which result in the the possession of defined sorption properties set out in the patent, namely, (1) a ratio of sorption of n-hexane to o-xylene, on a volume percent basis, of greater than 3, which sorption is determined at a P/P_0 of 0.1 and at a temperature of 50°C for n-hexane and 80°C for o-xylene and (2) by the ability of selectively cracking 3-methylpentane (3MP) in preference to the doubly branched 2,3-dimethylbutane (DMB) at 1000°F and 1 atmosphere pressure from a 1/1/1 weight ratio mixture of n-hexane/3-methyl-pentane/ 2,3-dimethylbutane, with the ratio of rate constants k_{3MP}/k_{DMB} determined at a temperature of 1000°F being in excess of 2. The expression, " P/P_0 ", is accorded its usual significance as described in the literature, for example, in "The Dynamical Character of Adsorption" by J.H. deBoer, 2nd Edition, Oxford University Press (1968) and is the relative pressure defined as the ratio of the partial pressure of sorbate to the vapor pressure of sorbate at the temperature of sorption. The ratio of the rate constants, k_{3MP}/k_{DMB} , is determined from 1st order kinetics, in the usual manner, by the following equation:

$$k = (1/T_c) \ln (1/1-\epsilon)$$

where k is the rate constant for each component, T_c is the contact time and ϵ is the fractional conversion of each component.

Zeolites conforming to these sorption requirements include the naturally occurring zeolite ferrierite as well as the known synthetic zeolites ZSM-22, ZSM-23 and ZSM-35. These zeolites are at least partly in the acid or hydrogen form when they are used in the dewaxing process and a metal hydrogenation component, preferably a noble metal such as platinum is preferable used.

Excellent results have been obtained with a Pt/ZSM-23 dewaxing catalyst.

5 The hydrocracking/hydroisomerization catalyst is a
bifunctional catalyst which comprises a mesoporous
crystalline material as described below as the
component which acts as a support and in addition,
provides the desired acidic functionality for the
hydrocracking reactions, together with a
hydrogenation-dehydrogenation component. The
10 hydrogenation-dehydrogenation component is provided by
a metal or combination of metals. Noble metals of
Group VIIIA, especially platinum and palladium may be
used where the level of sulfur and other contaminants
in the feed to the HDC/HDI step permits or,
15 alternatively, base metals may be used. Base metals of
Groups IVA, VIA and VIIIA, especially chromium,
molybdenum, tungsten, cobalt and nickel, may be used.
Base metal combinations, especially a combination of a
Group VIII A metal with Group IV A or VI A metal, such
20 as nickel-molybdenum, cobalt-nickel, nickel-tungsten,
cobalt-nickel-molybdenum and nickel-tungsten-titanium
are useful, although for certain applications platinum
is preferred.

25 The content of the metal component will vary
according to its catalytic activity. Thus, the highly
active noble metals may be used in smaller amounts than
the less active base metals. For example, 1 wt.% or
less platinum will be effective and in a preferred base
metal combination, 7 wt.% nickel and 2.1 to 40 wt.%
30 tungsten, expressed as metal. The present support
materials are, however, notable in that they are
capable of including a greater proportion of metal than
previous support materials because of their
extraordinarily large surface area. The metal

component may exceed 25 percent and still maintain a high surface area above $200 \text{ m}^2 \text{ g}^{-1}$. The hydrogenation component can be exchanged onto the support material, impregnated into it or physically admixed with it. If
5 the metal is to be impregnated into or exchanged onto the mesoporous support, it may be done, for example, by treating the zeolite with a platinum metal-containing ion. Suitable platinum compounds include
10 chloroplatinic acid, platinumous chloride and various compounds containing the platinum ammine complex. The metal compounds may be either compounds in which the metal is present in the cation of the compound and compounds in which it is present in the anion of the compound. Both types of compounds can be used.
15 Platinum compounds in which the metal is in the form of a cation of cationic complex, e.g., $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$ are particularly useful, as are anionic complexes such as the vanadate and metatungstate ions. Cationic forms of other metals are also very useful since they may be
20 exchanged onto the crystalline material or impregnated into it.

The acidic component of the hydrocracking/hydroisomerization catalyst is a mesoporous crystalline material which is described in
25 detail below. When it is used in the present catalysts, the mesoporous crystalline material is at least partly in the decationized or hydrogen form in order to provide the desired acidic functionality for the cracking reactions which are to take place.

30 The mesoporous catalytic material is an inorganic, porous, non-layered crystalline phase material which can be characterized (in its calcined form) by an X-ray diffraction pattern with at least one peak at a d-spacing greater than 18 Å with a relative intensity

of 100 and a benzene sorption capacity of greater than 15 grams of benzene per 100 grams of the material at 6.7 kPa (50 Torr) and 25°C.

5 The preferred form of the crystalline material has a hexagonal arrangement of uniformly-sized pores with a maximum perpendicular cross-section pore dimension of at least 1.3 nm (13 Å (Å)), and typically within the range of from 1.3 to 20 nm (13 Å to 200 Å). A preferred form of this hexagonal crystalline
10 composition, identified as MCM-41, exhibits a hexagonal electron diffraction pattern that can be indexed with a d_{100} value greater than 1.8 nm (18 Å), and a benzene adsorption capacity of greater than 15 grams benzene/100 grams crystal at 6.7 kPa (50 Torr) and
15 25°C. This material is described in detail in Serial No. 07/625,245 and below.

The inorganic, non-layered mesoporous crystalline material used as a component of the catalyst has the following composition:

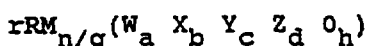
20 $M_{n/q}(W_a X_b Y_c Z_d O_h)$
wherein W is a divalent element, such as a divalent first row transition metal, e.g. manganese, cobalt and iron, and/or magnesium, preferably cobalt; X is a trivalent element, such as aluminum, boron, iron and/or
25 gallium, preferably aluminum; Y is a tetravalent element such as silicon and/or germanium, preferably silicon; Z is a pentavalent element, such as phosphorus; M is one or more ions, such as, for example, ammonium, Group IA, IIA and VIIB ions, usually
30 hydrogen, sodium and/or fluoride ions; n is the charge of the composition excluding M expressed as oxides; q is the weighted molar average valence of M; n/q is the number of moles or mole fraction of M; a, b, c, and d

are mole fractions of W, X, Y and Z, respectively; h is a number of from 1 to 2.5; and $(a+b+c+d) = 1$.

A preferred embodiment of the above crystalline material is when $(a+b+c)$ is greater than d, and $h = 2$.

5 A further embodiment is when a and d = 0, and $h = 2$. The preferred materials for use in making the present hydrocracking catalysts are the aluminosilicates.

10 In the as-synthesized form, the catalytic material has a composition, on an anhydrous basis, expressed empirically as follows:



where R is the total organic material not included in M as an ion, and r is the coefficient for R, i.e. the number of moles or mole fraction of R.

15 The M and R components are associated with the material as a result of their presence during crystallization, and are easily removed or, in the case of M, replaced by post-crystallization methods described below.

20 To the extent desired, the original M, e.g. sodium or chloride, ions of the as-synthesized material of this invention can be replaced in accordance with conventional ion-exchange techniques. Preferred replacing ions include metal ions, hydrogen ions, 25 hydrogen precursor, e.g. ammonium, ions and mixtures of these ions. Particularly preferred ions are those which provide the desired metal functionality in the final hydrocracking catalyst. These include hydrogen, rare earth metals and metals of Groups VIIA (e.g. Mn), VIIIA (e.g. Ni), IB (e.g. Cu), IVB (e.g. Sn) of the 30 Periodic Table of the Elements and mixtures of these ions.

The crystalline (i.e. having sufficient order to provide a diffraction pattern such as, for example, by

X-ray, electron or neutron diffraction, following calcination with at least one peak) mesoporous material may be characterized by its structure, which includes extremely large pore windows as well as by its high sorption capacity. The term "mesoporous" is used here to indicate crystals having uniform pores within the range of from 13 Å to 200 Å. The mesoporous materials have uniform pores within the range of from 13 Å to 200 Å, more usually from 15 Å to 100 Å. Since these pores are significantly larger than those of other crystalline materials, it is appropriate to refer to them as ultra-large pore size materials. For the purposes of this application, a working definition of "porous" is a material that adsorbs at least 1 gram of a small molecule, such as Ar, N₂, n-hexane or cyclohexane, per 100 grams of the solid.

The catalytic material can be distinguished from other porous inorganic solids by the regularity of its large open pores, whose pore size more nearly resembles that of amorphous or paracrystalline materials, but whose regular arrangement and uniformity of size (pore size distribution within a single phase of, for example, $\pm 25\%$, usually $\pm 15\%$ or less of the average pore size of that phase) resemble more those of crystalline framework materials such as zeolites. The preferred materials have a hexagonal arrangement of large open channels that can be synthesized with open internal diameters from 13 Å to 200 Å. The term "hexagonal" is intended to encompass not only materials that exhibit mathematically perfect hexagonal symmetry within the limits of experimental measurement, but also those with significant observable deviations from that ideal state. A working definition as applied to the microstructure of the present invention would be that

most channels in the material would be surrounded by six nearest neighbor channels at roughly the same distance. Defects and imperfections will cause significant numbers of channels to violate this criterion to varying degrees, depending on the quality of the material's preparation. Samples which exhibit as much as $\pm 25\%$ random deviation from the average repeat distance between adjacent channels still clearly give recognizable images of the present ultra-large pore materials. Comparable variations are also observed in the d_{100} values from the electron diffraction patterns.

The most regular preparations of the material of the present invention give an X-ray diffraction pattern with a few distinct maxima in the extreme low angle region. The positions of these peaks approximately fit the positions of the $hk0$ reflections from a hexagonal lattice. The X-ray diffraction pattern, however, is not always a sufficient indicator of the presence of these materials, as the degree of regularity in the microstructure and the extent of repetition of the structure within individual particles affect the number of peaks that will be observed. Indeed, preparations with only one distinct peak in the low angle region of the X-ray diffraction pattern have been found to contain substantial amounts of the material in them. Other techniques to illustrate the microstructure of this material are transmission electron microscopy and electron diffraction. Properly oriented specimens of the material show a hexagonal arrangement of large channels and the corresponding electron diffraction pattern gives an approximately hexagonal arrangement of diffraction maxima. The d_{100} spacing of the electron diffraction patterns is the distance between adjacent

spots on the hk0 projection of the hexagonal lattice and is related to the repeat distance a_0 between channels observed in the electron micrographs through the formula $d_{100} = a_0/\sqrt{3}$. This d_{100} spacing observed in the electron diffraction patterns corresponds to the d-spacing of a low angle peak in the X-ray diffraction pattern of the material. The most highly ordered preparations of the material obtained so far have 20-40 distinct spots observable in the electron diffraction patterns. These patterns can be indexed with the hexagonal hk0 subset of unique reflections of 100, 110, 200, 210, etc., and their symmetry-related reflections.

In its calcined form, the crystalline material may be further characterized by an X-ray diffraction pattern with at least one peak at a position greater than 18 Angstrom Units d-spacing ($4.909 \cdot 2_\theta$ for Cu K-alpha radiation) which corresponds to the d_{100} value of the electron diffraction pattern of the material, and an equilibrium benzene adsorption capacity of greater than 15 grams benzene/100 grams crystal at 50 torr and 25°C (basis: crystal material having been treated in an attempt to insure no pore blockage by incidental contaminants, if necessary).

The equilibrium benzene adsorption capacity characteristic of this material is measured on the basis of no pore blockage by incidental contaminants. For instance, the sorption test will be conducted on the crystalline material phase having any pore blockage contaminants and water removed by ordinary methods. Water may be removed by dehydration techniques, e.g. thermal treatment. Pore blocking inorganic amorphous materials, e.g. silica, and organics may be removed by contact with acid or base or other chemical agents such

that the detrital material will be removed without detrimental effect on the crystal.

5 More particularly, the calcined crystalline non-layered material may be characterized by an X-ray diffraction pattern with at least two peaks at positions greater than 10 Angstrom Units d-spacing (8.842 Å for Cu K-alpha radiation), at least one of which is at a position greater than 18 Angstrom Units d-spacing, and no peaks at positions less than 10 Å d-spacing with relative intensity greater than 20% of the strongest peak. Still more particularly, the X-ray diffraction pattern of the calcined material of this invention will have no peaks at positions less than 10 Å d-spacing with relative intensity greater than 10% of the strongest peak. In any event, at least one peak in the X-ray diffraction pattern will have a d-spacing that corresponds to the d_{100} value of the electron diffraction pattern of the material.

20 The calcined inorganic, non-layered crystalline material may also be characterized as having a pore size of 13 Å or greater as measured by physisorption measurements, described below. Pore size is considered a maximum perpendicular cross-section pore dimension of the crystal.

25 X-ray diffraction data were collected on a Scintag PAD X automated diffraction system employing theta-theta geometry, Cu K-alpha radiation, and an energy dispersive X-ray detector. Use of the energy dispersive X-ray detector eliminated the need for incident or diffracted beam monochromators. Both the incident and diffracted X-ray beams were collimated by double slit incident and diffracted collimation systems. The slit sizes used, starting from the X-ray tube source, were 0.5, 1.0, 0.3 and 0.2 mm,

respectively. Different slit systems may produce differing intensities for the peaks. The materials of the present invention that have the largest pore sizes may require more highly collimated incident X-ray beams in order to resolve the low angle peak from the transmitted incident X-ray beam.

The diffraction data were recorded by step-scanning at 0.04 degrees of 2θ , where θ is the Bragg angle, and a counting time of 10 seconds for each step. The interplanar spacings, d 's, were calculated in Å (Å), and the relative intensities of the lines, I/I_0 , where I_0 is one-hundredth of the intensity of the strongest line, above background, were derived with the use of a profile fitting routine. The intensities were uncorrected for Lorentz and polarization effects. The relative intensities are given in terms of the symbols vs = very strong (75-100), s = strong (50-74), m = medium (25-49) and w = weak (0-24). The diffraction data listed as single lines may consist of multiple overlapping lines which under certain conditions, such as very high experimental resolution or crystallographic changes, may appear as resolved or partially resolved lines. Typically, crystallographic changes can include minor changes in unit cell parameters and/or a change in crystal symmetry, without a substantial change in structure. These minor effects, including changes in relative intensities, can also occur as a result of differences in cation content, framework composition, nature and degree of pore filling, thermal and/or hydrothermal history, and peak width/shape variations due to particle size/shape effects, structural disorder or other factors known to those skilled in the art of X-ray diffraction.

The equilibrium benzene adsorption capacity is determined by contacting the material of the invention, after dehydration or calcination at, for example, 540°C for at least one hour and other treatment, if
5 necessary, in an attempt to remove any pore blocking contaminants, at 25°C and 50 torr benzene until equilibrium is reached. The weight of benzene sorbed is then determined as described below.

The ammonium form of the catalytic material may be
10 readily converted to the hydrogen form by thermal treatment (calcination). This thermal treatment is generally performed by heating one of these forms at a temperature of at least 400°C for at least 1 minute and generally not longer than 20 hours, preferably from 1.
15 to 10 hours. While subatmospheric pressure can be employed for the thermal treatment, atmospheric pressure is desired for reasons of convenience, such as in air, nitrogen, ammonia, etc. The thermal treatment can be performed at a temperature up to 750°C. The
20 thermally treated product is particularly useful in the catalysis of certain hydrocarbon conversion reactions.

The crystalline material can be prepared by one of several methods, each with particular limitations.

A first method involves a reaction mixture having
25 an X_2O_3/YO_2 mole ratio of from 0 to 0.5, but an Al_2O_3/SiO_2 mole ratio of from 0 to 0.01, a crystallization temperature of from 25°C to 250°C, preferably from 50°C to 175°C, and an organic directing agent, hereinafter more particularly described, or,
30 preferably a combination of that organic directing agent plus an additional organic directing agent, described below. This first method comprises preparing a reaction mixture containing sources of, for example, alkali or alkaline earth metal (M), e.g. sodium or

potassium, cation if desired, one or a combination of oxides selected from the group consisting of divalent element W, e.g. cobalt, trivalent element X, e.g. aluminum, tetravalent element Y, e.g. silicon, and pentavalent element Z, e.g. phosphorus, an organic (R) directing agent, described below, and a solvent or solvent mixture, such as, for example, C₁-C₆ alcohols, C₁-C₆ diols and/or water, especially water. The reaction mixture has a composition, in terms of mole ratios of oxides, within the following ranges:

	<u>Reactants</u>	<u>Useful</u>	<u>Preferred</u>
	X ₂ O ₃ /YO ₂	0 to 0.5	0.001 to 0.5
	Al ₂ O ₃ /SiO ₂	0 to 0.01	0.001 to 0.01
	X ₂ O ₃ /(YO ₂ +Z ₂ O ₅)	0.1 to 100	0.1 to 20
15	X ₂ O ₃ /(YO ₂ +WO+Z ₂ O ₅)	0.1 to 100	0.1 to 20
	Solvent/ (YO ₂ +WO+Z ₂ O ₅ +X ₂ O ₃)	1 to 1500	5 to 1000
	OH ⁻ /YO ₂	0 to 10	0 to 5
	(M ₂ /e ^O +R ₂ /f ^O)/ (YO ₂ +WO+Z ₂ O ₅ +X ₂ O ₃)	0.01 to 20	0.05 to 5
20	M ₂ /e ^O / (YO ₂ +WO+Z ₂ O ₅ +X ₂ O ₃)	0 to 10	0 to 5
	R ₂ /f ^O / (YO ₂ +WO+Z ₂ O ₅ +X ₂ O ₃)	0.01 to 2.0	0.03 to 1.0

25 where e and f are the weighted average valences of M and R, respectively.

In this first method, when no Z and/or W oxides are added to the reaction mixture, the pH is important and must be maintained at from 9 to 14. When Z and/or W oxides are present in the reaction mixture, the pH is not narrowly important for synthesis of the present crystalline material. In this, as well as the following methods for synthesis of the present material the R₂/f^O/(YO₂+WO+Z₂O₅+X₂O₃) ratio is important. When

this ratio is less than 0.01 or greater than 2.0, impurity products tend to be synthesized at the expense of the desired crystalline material.

5 A second method for synthesis of the crystalline material involves a reaction mixture having an X_2O_3/YO_2 mole ratio of from 0 to 0.5, a crystallization temperature of from 25° to 250°C, preferably from 50° to 175°C, and two separate organic directing agents, i.e. the organic and additional organic directing
10 agents, described below. This second method comprises preparing a reaction mixture containing sources of, for example, alkali or alkaline earth metal (M), e.g. sodium or potassium, cation if desired, one or a combination of oxides selected from the group
15 consisting of divalent element W, e.g. cobalt, trivalent element X, e.g. aluminum, tetravalent element Y, e.g. silicon, and pentavalent element Z, e.g. phosphorus, a combination of organic directing agent and additional organic directing agent (R), each
20 described below, and a solvent or solvent mixture, such as, for example, C_1-C_6 alcohols, C_1-C_6 diols and/or water, especially water. The reaction mixture has a composition, in terms of mole ratios of oxides, within the following ranges:

	<u>Reactants</u>	<u>Useful</u>	<u>Preferred</u>
	X_2O_3/YO_2	0 to 0.5	0.001 to 0.5
	$X_2O_3/(YO_2+Z_2O_5)$	0.1 to 100	0.1 to 20
	$X_2O_3/(YO_2+WO+Z_2O_5)$	0.1 to 100	0.1 to 20
5	Solvent/ $(YO_2+WO+Z_2O_5+X_2O_3)$	1 to 1500	5 to 1000
	OH^-/YO_2	0 to 10	0 to 5
	$(M_2/e^{O+R_2/f^O})/$ $(YO_2+WO+Z_2O_5+X_2O_3)$	0.01 to 20	0.05 to 5
10	$M_2/e^O/$ $(YO_2+WO+Z_2O_5+X_2O_3)$	0 to 10	0 to 5
	$R_2/f^O/$ $(YO_2+WO+Z_2O_5+X_2O_3)$	0.1 to 2.0	0.12 to 1.0

where e and f are the weighted average valences of M and R, respectively.

In this second method, when no Z and/or W oxides are added to the reaction mixture, the pH is important and must be maintained at from 9 to 14. When Z and/or W oxides are present in the reaction mixture, the precise value of the pH is not important for crystallization.

A third method for synthesis of the crystalline material is where X comprises aluminum and Y comprises silicon, the crystallization temperature must be from 25° to 175°C, preferably from 50° to 150°C, and an organic directing agent, described below, or, preferably a combination of that organic directing agent plus an additional organic agent, described below, is used. This third method comprises preparing a reaction mixture containing sources of, for example, alkali or alkaline earth metal (M), e.g. sodium or potassium, cation if desired, one or more sources of aluminum and/or silicon, an organic (R) directing

agent, hereinafter more particularly described, and a solvent or solvent mixture, such as, for example C₁-C₆ alcohols, C₁-C₆ diols and/or water, especially water. The reaction mixture has a composition, in terms of mole ratios of oxides, within the following ranges:

	<u>Reactants</u>	<u>Useful</u>	<u>Preferred</u>
	Al ₂ O ₃ /SiO ₂	0 to 0.5	0.001 to 0.5
	Solvent/SiO ₂	1 to 1500	5 to 1000
	OH ⁻ /SiO ₂	0 to 10	0 to 5
5			
10	(M ₂ /e ^O +R ₂ /f ^O)/ (SiO ₂ +Al ₂ O ₃)	0.01 to 20	0.05 to 5
	M ₂ /e ^O / (SiO ₂ +Al ₂ O ₃)	0 to 5	0 to 3
	R ₂ /f ^O / (SiO ₂ +Al ₂ O ₃)	0.01 to 2	0.03 to 1
15			

where e and f are the weighted average valences of M and R, respectively.

In this third method, the pH is important and must be maintained at from 9 to 14. This method involves the following steps:

- (1) Mix the organic (R) directing agent with the solvent or solvent mixture such that the mole ratio of solvent/R₂/f^O is within the range of from 50 to 800, preferably from 50 to 500. This mixture constitutes the "primary template" for the synthesis method.
- (2) To the primary template mixture of step (1) add the sources of oxides, e.g. silica and/or alumina such that the ratio of R₂/f^O/(SiO₂+Al₂O₃) is within the range of from 0.01 to 2.0.
- (3) Agitate the mixture resulting from step (2) at a temperature of from 20°C to 40°C, preferably for from 5 minutes to 3 hours.

(4) Allow the mixture to stand with or without agitation, preferably at a temperature of from 20° to 100°C, and preferably for from 10 minutes to 24 hours.

5 (5) Crystallize the product from step (4) at a temperature of from 50° to 175°C, preferably for from 1 hour to 72 hours. Crystallization temperatures higher in the given ranges are most preferred.

10 A fourth method for the present synthesis involves the reaction mixture used for the third method, but the following specific procedure with tetraethylorthosilicate the source of silicon oxide:

15 (1) Mix the organic (R) directing agent with the solvent or solvent mixture such that the mole ratio of solvent/ $R_{2/f}O$ is within the range of from 50 to 800, preferably from 50 to 500. This mixture constitutes the "primary template" for the synthesis method.

20 (2) Mix the primary template mixture of step (1) with tetraethylorthosilicate and a source of aluminum oxide, if desired, such that the $R_{2/f}O/SiO_2$ mole ratio is in the range of from 0.5 to 2.0.

25 (3) Agitate the mixture resulting from step (2) for from 10 minutes to 6 hours, preferably from 30 minutes to 2 hours, at a temperature of from 0° to 25°C, and a pH of less than 12. This step permits hydrolysis/polymerization to take place and the resultant mixture will appear cloudy.

30 (4) Crystallize the product from step (3) at a temperature of from 25° to 150°C, preferably from

95° to 110°C, for from 4 to 72 hours, preferably from 16 to 48 hours.

In each of the above methods, batch crystallization of the crystalline material can be carried out under either static or agitated, e.g. stirred, conditions in a suitable reactor vessel, such as for example, polypropylene jars or teflon lined or stainless steel autoclaves. Crystallization may also be conducted continuously in suitable equipment. The total useful range of temperatures for crystallization is noted above for each method for a time sufficient for crystallization to occur at the temperature used, e.g. from 5 minutes to 14 days. The crystals are then separated from the liquid and recovered. Following the synthesis, the crystalline material should be subjected to treatment to remove part or all of any organic constituent.

When a source of silicon is used in the synthesis method, it is preferred to use at least in part an organic silicate, such as, for example, a quaternary ammonium silicate. Non-limiting examples of such a silicate include tetramethylammonium silicate and tetraethylorthosilicate.

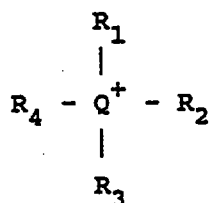
By adjusting conditions of the synthesis reaction for each method, like temperature, pH and time of reaction, etc., within the above limits, various embodiments of the present non-layered crystalline material with a desired average pore size may be prepared. In particular, changing the pH, the temperature or the reaction time may promote formation of product crystals with different average pore size.

Non-limiting examples of various combinations of W, X, Y and Z contemplated for the first and second synthesis methods include:

	<u>W</u>	<u>X</u>	<u>Y</u>	<u>Z</u>
	--	Al	Si	--
	--	Al	--	P
	--	Al	Si	P
5	Co	Al	--	P
	Co	Al	Si	P
	--	--	Si	--

including the combinations of W being Mg, or an element selected from the divalent first row transition metals, e.g. Mn, Co and Fe; X being B, Ga or Fe; and Y being Ge.

An organic directing agent for use in each of the above methods for synthesizing the present material from the respective reaction mixtures is an ammonium or phosphonium ion of the formula $R_1R_2R_3R_4Q^+$, i.e.:



where Q is nitrogen or phosphorus and wherein at least one of R_1 , R_2 , R_3 and R_4 is aryl or alkyl of from 6 to 36 carbon atoms, e.g. $-C_6H_{13}$, $-C_{10}H_{21}$, $-C_{16}H_{33}$ and $-C_{18}H_{37}$, or combinations thereof, the remainder of R_1 , R_2 , R_3 and R_4 being selected from hydrogen, alkyl of from 1 to 5 carbon atoms and combinations of these. The compound from which the above ammonium or phosphonium ion is derived may be, for example, the hydroxide, halide, silicate, or mixtures of these.

In the first and third methods above it is preferred to have an additional organic directing agent and in the second method it is required to have a combination of the above organic directing agent and an additional organic directing agent. That additional

organic directing agent is the ammonium or phosphonium ion of the above directing agent formula wherein R_1 , R_2 , R_3 and R_4 together or separately are selected from the group consisting of hydrogen and alkyl of 1 to 5 carbon atoms and combinations thereof. Any such combination of organic directing agents go to make up "R" and will be in molar ratio of 100/1 to 0.01/1, first above listed organic directing agent/additional organic directing agent.

The particular effectiveness of the required directing agent, when compared with other such agents known to direct synthesis of one or more other crystal structures, is believed due to its ability to function as a template in the above reaction mixture in the nucleation and growth of the desired ultra-large pore crystals with the limitations discussed above. Non-limiting examples of these directing agents include cetyltrimethylammonium, cetyltrimethylphosphonium, benzyltrimethylammonium, cetylpyridinium, myristyltrimethylammonium, decyltrimethylammonium, dodecyltrimethylammonium and dimethyldidodecylammonium.

The reaction mixture components can be supplied by more than one source. The reaction mixture can be prepared either batchwise or continuously. Crystal size and crystallization time of the new crystalline material will vary with the nature of the reaction mixture employed and the crystallization conditions.

The crystals prepared by the synthesis procedure can be shaped into a wide variety of particle sizes. Generally speaking, the particles can be in the form of a powder, a granule, or a molded product, such as an extrudate having particle size sufficient to pass through a 2 mesh (Tyler) screen and be retained on a 400 mesh (Tyler) screen. In cases where the catalyst

is molded, such as by extrusion, the crystals can be extruded before drying or partially dried and then extruded.

5 The size of the pores in the present mesoporous catalytic materials is large enough that the
spatiospecific selectivity with respect to transition
state species in reactions such as cracking is
minimized (Chen et al., "Shape Selective Catalysis in
Industrial Applications", 36 CHEMICAL INDUSTRIES, pgs.
10 41-61 (1989) to which reference is made for a
discussion of the factors affecting shape selectivity).
Diffusional limitations are also minimized as a result
of the very large pores. For these reasons, the
present compositions are especially useful for
15 catalyzing the hydrocracking reactions with high
boiling feeds containing components with bulky
molecular configurations.

It is normally preferred to use the crystalline
material in a form which has sufficient acidic
20 functionality to give it an alpha value of 1 or more.
The alpha test is described in U.S. Patent No.
3,354,078 and in J. Catalysis, 4, 527 (1965); 6, 278
(1966); and 61, 395 (1980), to which reference is made
for a description of the test. The experimental
25 conditions of the test used to determine the alpha
values referred to in this specification include a
constant temperature of 538°C and a variable flow rate
as described in detail in J. Catalysis, 61, 395 (1980).
The acidic functionality may be controlled by base
30 exchange, especially with alkali metal cations such as
sodium, by steaming or by control of the silica:alumina
ratio of the material.

It may be desirable to incorporate the catalyst in
another material resistant to the temperature and other

conditions employed in the process. Such matrix materials include synthetic and naturally occurring substances such as inorganic materials, e.g. clay, silica and metal oxides. Matrix materials may themselves possess catalytic properties, generally of an acidic nature.

The catalyst may be treated by conventional pre-sulfiding treatments, e.g. by heating in the presence of hydrogen sulfide, to convert oxide forms of the metals such as CoO or NiO to their corresponding sulfides.

Examples 1 to 19 below illustrate the preparation of the mesoporous crystalline materials used to prepare the catalysts. In these examples, the sorption data for water, cyclohexane, benzene and/or n-hexane, they are Equilibrium Adsorption values determined as follows:

A weighed sample of the adsorbent, after calcination at 540°C for at least 1 hour and other treatment, if necessary, to remove any pore blocking contaminants, is contacted with the desired pure adsorbate vapor in an adsorption chamber. The increase in weight of the adsorbent is calculated as the adsorption capacity of the sample in terms of grams/100 grams adsorbent based on adsorbent weight after calcination at 540°C. The present composition exhibits an equilibrium benzene adsorption capacity at 6.7 kPa (50 Torr) and 25°C of greater than 15 grams/100 grams, particularly greater than 17.5 g/100 g/ and more particularly greater than 20 g/100 g.

A preferred way to do this is to contact the desired pure adsorbate vapor in an adsorption chamber evacuated to less than 1 mm at conditions of 12 Torr of water vapor, 40 Torr of n-hexane or cyclohexane vapor,

or 6.7 kPa) (50 Torr) of benzene vapor, at 25°C. The pressure is kept constant (within ± 0.5 mm) by addition of adsorbate vapor controlled by a manostat during the adsorption period. As adsorbate is adsorbed by the new crystal, the decrease in pressure causes the manostat to open a valve which admits more adsorbate vapor to the chamber to restore the above control pressures. Sorption is complete when the pressure change is not sufficient to activate the manostat.

Another way of doing this for benzene adsorption data is on a suitable thermogravimetric analysis system, such as a computer-controlled 990/951 duPont TGA system. The adsorbent sample is dehydrated (physically sorbed water removed) by heating at, for example, 350° or 500°C to constant weight in flowing helium. If the sample is in as-synthesized form, e.g. containing organic directing agents, it is calcined at 540°C in air and held to constant weight instead of the previously described 350° or 500°C treatment. Benzene adsorption isotherms are measured at 25°C by blending a benzene saturated helium gas stream with a pure helium gas stream in the proper proportions to obtain the desired benzene partial pressure. The value of the adsorption at 6.7 kPa (50 Torr) of benzene is taken from a plot of the adsorption isotherm.

In the examples, percentages are by weight unless otherwise indicated.

Example 1

One hundred grams of cetyltrimethylammonium (CTMA) hydroxide solution, prepared by contacting a 29 wt.% N,N,N- trimethyl-1-hexadecanaminium chloride solution with a hydroxide-for-halide exchange resin, was combined with 100 grams of an aqueous solution of tetramethylammonium (TMA) silicate (10% silica) with

5 stirring. Twenty-five grams of HiSil, a precipitated hydrated silica containing 6 wt.% free water and 4.5 wt.% bound water of hydration and having an ultimate particle size of 0.02 micron, was added. The resulting mixture was placed in a polypropylene bottle, which was kept in a steam box at 95°C overnight. The mixture had a composition in terms of moles per mole Al_2O_3 :

10 2.7 moles Na_2O
392 moles SiO_2
35.7 moles $(\text{CTMA})_2\text{O}$
61.7 moles $(\text{TMA})_2\text{O}$
6231 moles H_2O

15 The resulting solid product was recovered by filtration and dried in air at ambient temperature. The product was then calcined at 540°C for 1 hour in nitrogen, followed by 6 hours in air.

The calcined product proved to have a surface area of 475 m^2/g and the following equilibrium adsorption capacities in grams/100 grams:

20 H_2O 8.3
Cyclohexane 22.9
n-Hexane 18.2
Benzene 21.5

25 The product of this example may be characterized by X-ray diffraction as including a very strong relative intensity line at 37.8 ± 2.0 Å d-spacing, and weak lines at 21.6 ± 1.0 and 19.2 ± 1.0 Å. Transmission electron microscopy (TEM) produced images of a hexagonal arrangement of uniform pores and hexagonal electron diffraction pattern with a d_{100} value of 39 Å.

Example 2

30 One hundred grams of cetyltrimethylammonium (CTMA) hydroxide solution prepared as in Example 1 was

combined with 100 grams of an aqueous solution of tetramethylammonium (TMA) hydroxide (25%) with stirring. Twenty-five grams of HiSil, a precipitated hydrated silica containing 6 wt.% free water and 4.5 wt.% bound water of hydration and having an ultimate particle size of 0.02 micron, was added. The resulting mixture was placed in a static autoclave at 150°C overnight. The mixture had a composition in terms of moles per mole Al_2O_3 :

2.7 moles Na_2O
291 moles SiO_2
35.7 moles $(\text{CTMA})_2\text{O}$
102 moles $(\text{TMA})_2\text{O}$
6120 moles H_2O

The resulting solid product was recovered by filtration and dried in air at ambient temperature. The product was then calcined at 540°C for 1 hour in nitrogen, followed by 6 hours in air.

The calcined product proved to have a surface area of 993 m^2/g and the following equilibrium adsorption capacities in grams/100 grams:

H_2O	7.1
Cyclohexane	47.2
n-Hexane	36.2
Benzene	49.5

The X-ray diffraction pattern of the calcined product may be characterized as including a very strong relative intensity line at 39.3 ± 2.0 Å d-spacing, and weak lines at 22.2 ± 1.0 and 19.4 ± 1.0 Å. TEM indicated that the product contained the ultra-large pore material.

A portion of the above product was then contacted with 100% steam at 788°C (1450°F) for two hours. The surface area of the steamed material was measured to be

440 m²/g, indicating that 45% was retained following severe steaming.

5 Another portion of the calcined product of this example was contacted with 100% steam at 677°C (1250°F) for two hours. The surface area of this material was measured to be 718 m²/g, indicating that 72% was retained after steaming at these conditions.

Example 3

10 Water, cetyltrimethylammonium hydroxide solution prepared as in Example 1, aluminum sulfate, HiSil and an aqueous solution of tetrapropylammonium (TPA) bromide (35%) were combined to produce a mixture having a composition in terms of moles per mole Al₂O₃:

15 0.65 moles Na₂O
65 moles SiO₂
8.8 moles (CTMA)₂O
1.22 moles (TPA)₂O
1336 moles H₂O

20 The resulting mixture was placed in a polypropylene bottle, which was kept in a steam box at 95°C for 192 hours. The sample was then cooled to room temperature and combined with CTMA hydroxide solution prepared as in Example 1 and TMA hydroxide (25% by weight) in the weight ratio of 3 parts mixture, 1 part
25 CTMA hydroxide and 2 parts TMA hydroxide. The combined mixture was then placed in a polypropylene bottle and kept in a steam box at 95°C overnight. The combined

mixture had a composition in terms of moles per mole Al_2O_3 :

5 0.65 moles Na_2O
 65 moles SiO_2
 15 moles $(\text{CTMA})_2\text{O}$
 1.22 moles $(\text{TPA})_2\text{O}$
 35.6 moles $(\text{TMA})_2\text{O}$
 2927 moles H_2O

10 The resulting solid product was recovered by
 filtration and dried in air at ambient temperature.
 The product was then calcined at 540°C for 1 hour in
 nitrogen, followed by 6 hours in air.

15 The calcined product proved to have a surface area
 of $1085 \text{ m}^2/\text{g}$ and the following equilibrium adsorption
 capacities in grams/100 grams:

H_2O	11.5
Cyclohexane	> 50
n-Hexane	39.8
Benzene	62

20 The X-ray diffraction pattern of the calcined
 product of this example may be characterized as
 including a very strong relative intensity line at 38.2
 $\pm 2.0 \text{ \AA}$ d-spacing, and weak lines at 22.2 ± 1.0 and
 $19.4 \pm 1.0 \text{ \AA}$. TEM indicated the product contained the
25 ultra-large pore material.

Example 4

30 Two hundred grams of cetyltrimethylammonium (CTMA)
 hydroxide solution prepared as in Example 1 was
 combined with 2 grams of Catapal alumina (alpha-alumina
 monohydrate, 74% alumina) and 100 grams of an aqueous
 solution of tetramethylammonium (TMA) silicate (10%
 silica) with stirring. Twenty-five grams of HiSil, a
 precipitated hydrated silica containing 6 wt.% free
 water and 4.5 wt.% bound water of hydration and having

an ultimate particle size of 0.02 micron, was added. The resulting mixture was placed in a static autoclave at 150°C for 48 hours. The mixture had a composition in terms of moles per mole Al_2O_3 :

5 0.23 moles Na_2O
 33.2 moles SiO_2
 6.1 moles $(\text{CTMA})_2\text{O}$
 5.2 moles $(\text{TMA})_2\text{O}$
 780 moles H_2O

10 The resulting solid product was recovered by filtration and dried in air at ambient temperature. The product was then calcined at 540°C for 1 hour in nitrogen, followed by 6 hours in air.

15 The calcined product proved to have a surface area of 1043 m^2/g and the following equilibrium adsorption capacities in grams/100 grams:

H_2O 6.3
 Cyclohexane > 50
 n-Hexane 49.1
20 Benzene 66.7

 The X-ray diffraction pattern of the calcined product may be characterized as including a very strong relative intensity line at 40.8 ± 2.0 Å d-spacing, and weak lines at 23.1 ± 1.0 and 20.1 ± 1.0 Å. TEM
25 indicated that the product contained the ultra-large pore material.

Example 5

 Two-hundred sixty grams of water was combined with 77 grams of phosphoric acid (85%), 46 grams of Catapal alumina (74% alumina), and 24 grams of pyrrolidine
30 (Pyr) with stirring. This first mixture was placed in a stirred autoclave and heated to 150°C for six days. The material was filtered, washed and air-dried. Fifty grams of this product was slurried with 200 grams of

water and 200 grams of cetyltrimethylammonium hydroxide solution prepared as in Example 1. Four hundred grams of an aqueous solution of tetraethylammonium silicate (10% silica) was then added to form a second mixture which was placed in a polypropylene bottle and kept in a steam box at 95°C overnight. The first mixture had a composition in terms of moles per mole Al_2O_3 :

1.0 moles P_2O_5
0.51 moles $(\text{Pyr})_2\text{O}$
47.2 moles H_2O

The resulting solid product was recovered by filtration and dried in air at ambient temperature. The product was then calcined at 540°C for 1 hour in nitrogen, followed by 6 hours in air.

The calcined product proved to have a surface area of 707 m^2/g and the following equilibrium adsorption capacities in grams/100 grams:

H_2O	33.2
Cyclohexane	19.7
n-Hexane	20.1
Benzene	23.3

The X-ray diffraction pattern of the calcined product may be characterized as including a very strong relative intensity line at 25.4 ± 1.5 Å d-spacing. TEM indicated the product contained the present ultra-large pore material.

Example 6

A solution of 1.35 grams of NaAlO_2 (43.5% Al_2O_3 , 30% Na_2O) dissolved in 45.2 grams of water was mixed with 17.3 grams of NaOH , 125.3 grams of colloidal silica (40%, Ludox HS-40) and 42.6 grams of 40% aqueous solution of tetraethylammonium (TEA) hydroxide. After stirring overnight, the mixture was heated for 7 days in a steam box (95°C). Following filtration, 151 grams

of this solution was mixed with 31 grams of cetyltrimethylammonium hydroxide solution prepared as in Example 1 and stored in the steam box at 95°C for 13 days. The mixture had the following relative molar composition:

5

0.25 moles Al_2O_3
10 moles Na_2O
36 moles SiO_2
0.95 moles $(\text{CTMA})_2\text{O}$
2.5 moles $(\text{TEA})_2\text{O}$
445 moles H_2O

10

The resulting solid product was recovered by filtration and washed with water and ethanol. The product was then calcined at 540°C for 1 hour in nitrogen, followed by 6 hours in air.

15

The calcined product composition included 0.14 wt.% Na, 68.5 wt.% SiO_2 and 5.1 wt.% Al_2O_3 , and proved to have a benzene equilibrium adsorption capacity of 58.6 grams/100 grams.

20

The X-ray diffraction pattern of the calcined product may be characterized as including a very strong relative intensity line at 31.4 ± 1.5 Å d-spacing. TEM indicated that the product contained the present ultra-large pore material.

25

Example 7

A mixture of 300 grams of cetyltrimethylammonium (CTMA) hydroxide solution prepared as in Example 1 and 41 grams of colloidal silica (40%, Ludox HS-40) was heated in a 600 cc autoclave at 150°C for 48 hours with stirring at 200 rpm. The mixture has a composition in terms of moles per mole SiO_2 :

30

0.5 mole $(\text{CTMA})_2\text{O}$
46.5 moles H_2O

The resulting solid product was recovered by filtration, washed with water, then calcined at 540°C for 1 hour in nitrogen, followed by 10 hours in air.

5 The calcined product composition included less than 0.01 wt.% Na, 98.7 wt.% SiO₂ and 0.01 wt.% Al₂O₃, and proved to have a surface area of 896 m²/g. The calcined product had the following equilibrium adsorption capacities in grams/100 grams:

	H ₂ O	8.4
10	Cyclohexane	49.8
	n-Hexane	42.3
	Benzene	55.7

The X-ray diffraction pattern of the calcined product of this example may be characterized as including a very strong relative intensity line at 40.0 ± 2.0 Å d-spacing and a weak line at 21.2 ± 1.0 Å. TEM indicated that the product of this example contained at least three separate phases, one of which was the ultra-large pore material.

20 Example 8

A mixture of 150 grams of cetyltrimethylammonium (CTMA) hydroxide solution prepared as in Example 1 and 21 grams of colloidal silica (40%, Ludox HS-40) with an initial pH of 12.64 was heated in a 300 ml autoclave at 150°C for 48 hours with stirring at 200 rpm. The mixture had a composition in terms of moles per mole SiO₂:

0.5 mole (CTMA)₂O
46.5 moles H₂O

30 The resulting solid product was recovered by filtration, washed with water, then calcined at 540°C for 6 hours in air.

The calcined product composition was measured to include 0.01 wt.% Na, 93.2 wt.% SiO₂ and 0.016 wt.%

Al_2O_3 , and proved to have a surface area of $992 \text{ m}^2/\text{g}$ and the following equilibrium adsorption capacities in grams/100 grams:

	H_2O	4.6
5	Cyclohexane	> 50
	n-Hexane	> 50
	Benzene	62.7

The X-ray diffraction pattern of the calcined product may be characterized as including a very strong relative intensity line at $43.6 \pm 2.0 \text{ \AA}$ d-spacing and weak lines at 25.1 ± 1.5 and $21.7 \pm 1.0 \text{ \AA}$. TEM indicated that the product contained the ultra-large pore material.

Example 9

15 Sodium aluminate (4.15g) was added slowly into a solution containing 16g of myristyltrimethylammonium bromide ($\text{C}_{14}\text{TMABr}$) in 100g of water. Tetramethylammonium silicate (100g-10% SiO_2), HiSil (25g) and tetramethylammonium hydroxide (14.2g-25% solution) were then added to the mixture. The mixture was crystallized in an autoclave at 120°C with stirring for 24 hours.

25 The product was filtered, washed and air dried. Elemental analysis showed the product contained 53.3 wt.% SiO_2 , 3.2 wt.% Al_2O_3 , 15.0 wt.% C, 1.88 wt.% N, 0.11 wt.% Na and 53.5 wt.% ash at 1000°C . The X-ray diffraction pattern of the material after calcination at 540°C for 1 hour in N_2 and 6 hours in air includes a very strong relative intensity line at $35.3 \pm 2.0 \text{ \AA}$ d-spacing and weak lines at 20.4 ± 1.0 and $17.7 \pm 1.0 \text{ \AA}$ d-spacing. TEM indicated that the product contained the ultra-large pore material.

30 The washed product, having been exchanged with 1N ammonium nitrate solution at room temperature, then

calcined, proved to have a surface area of $827 \text{ m}^2/\text{g}$ and the following equilibrium adsorption capacities in g/100g anhydrous sorbent:

	H_2O	30.8
5	Cyclohexane	33.0
	n-Hexane	27.9
	Benzene	40.7

Example 10

Sodium aluminate (8.3g) was added slowly into a solution containing 184g of dodecyltrimethylammonium hydroxide ($\text{C}_{12}\text{TMAOH}$, 50%) solution diluted with 480g of water. UltraSil (50g) and an aqueous solution of tetramethylammonium silicate (200g-10% SiO_2) and tetramethylammonium hydroxide (26.38g-25% solution) were then added to the mixture. The mixture was crystallized in an autoclave at 100°C with stirring for 24 hours.

The product was filtered, washed and air dried. After calcination at 540°C for 1 hour in N_2 and 6 hours in air, the X-ray diffraction pattern includes a very strong relative intensity line at $30.4 \pm 1.5 \text{ \AA}$ d-spacing and weak lines at 17.7 ± 1.0 and $15.3 \pm 1.0 \text{ \AA}$ d-spacing. TEM indicated that the product contained the ultra-large pore material.

The washed product, having been exchanged with 1N ammonium nitrate solution at room temperature, then calcined, proved to have a surface area of $1078 \text{ m}^2/\text{g}$ and the following equilibrium adsorption capacities in g/100g anhydrous sorbent:

	H_2O	32.6
	Cyclohexane	38.1
	n-Hexane	33.3
30	Benzene	42.9

Example 11

5 A solution of 4.9 grams of NaAlO_2 (43.5 % Al_2O_3 , 30% NaO_2) in 37.5 grams of water was mixed with 46.3 cc of 40% aqueous tetraethylammonium hydroxide solution and 96 grams of colloidal silica (40%, Ludox HS-40). The gel was stirred vigorously for 0.5 hour, mixed with an equal volume (150 ml) of cetyltrimethylammonium hydroxide solution prepared as in Example 1 and reacted at 100°C for 168 hours. The mixture had the following composition in terms of moles per mole Al_2O_3 :

10 1.1 moles Na_2O
30.6 moles SiO_2
3.0 moles $(\text{TEA})_2\text{O}$
3.25 moles $(\text{CTMA})_2\text{O}$
15 609 moles H_2O

The resulting solid product was recovered by filtration, washed with water then calcined at 540°C for 16 hours in air. The calcined product proved to have a surface area of 1352 m^2/g and the following equilibrium adsorption capacities in grams/100 grams:

20

H_2O	23.6
Cyclohexane	>50
n-Hexane	49
Benzene	67.5

25 The X-ray diffraction pattern of the calcined product may be characterized as including a very strong relative intensity line at 38.5 ± 2.0 Å d-spacing and a weak line at 20.3 ± 1.0 Å. TEM indicated that the product contained the ultra-large pore material.

30 Example 12

Two hundred grams of cetyltrimethylammonium (CTMA) hydroxide solution prepared as in Example 1 was combined with 4.15 grams of sodium aluminate and 100 grams of aqueous tetramethylammonium (TMA) silicate

solution (10% silica) with stirring. Twenty-five grams of HiSil, a precipitated hydrated silica containing 6 wt.% free water and 4.5 wt.% bound water of hydration and having an ultimate particle size of 0.02 micron, was added. The resulting mixture was placed in a static autoclave at 150°C for 24 hours. The mixture had a composition in terms of moles per mole Al_2O_3 :

1.25 moles Na_2O
27.8 moles SiO_2
5.1 moles $(\text{CTMA})_2\text{O}$
4.40 moles $(\text{TMA})_2\text{O}$
650 moles H_2O

The resulting solid product was recovered by filtration and dried in air at ambient temperature. The product was then calcined at 540°C for 1 hour in nitrogen, followed by 6 hours in air. TEM indicated that this product contained the ultra-large pore material. The X-ray diffraction pattern of The calcined product of this example can be characterized as including a very strong relative intensity line at 44.2 ± 2.0 Å d-spacing and weak lines at 25.2 ± 1.5 and 22.0 ± 1.0 Å.

The calcined product proved to have a surface area of 932 m^2/g and the following equilibrium adsorption capacities in grams/100 grams:

H_2O	39.3
Cyclohexane	46.6
n-Hexane	37.5
Benzene	50

Example 13

Two hundred grams of cetyltrimethylammonium (CTMA) hydroxide solution prepared as in Example 1 was combined with 4.15 grams of sodium aluminate and 100 grams of aqueous tetramethylammonium (TMA) silicate

solution (10% silica) with stirring. Twenty-five grams of HiSil, a precipitated hydrated silica containing 6 wt.% free water and 4.5 wt.% bound water of hydration and having an ultimate particle size of 0.02 micron, was added. The resulting mixture was placed in a steam box at 100°C for 48 hours. The mixture had a composition in terms of moles per mole Al_2O_3 :

1.25 moles Na_2O
27.8 moles SiO_2
5.1 moles $(\text{CTMA})_2\text{O}$
4.4 moles $(\text{TMA})_2\text{O}$
650 moles H_2O

The resulting solid product was recovered by filtration and dried in air at ambient temperature. The product was then calcined at 540°C for 1 hour in nitrogen, followed by 6 hours in air. The calcined product proved to have the following equilibrium adsorption capacities in grams/100 grams:

H_2O	35.2
Cyclohexane	> 50
n-Hexane	40.8
Benzene	53.5

The X-ray diffraction pattern of the calcined product may be characterized as including a very strong relative intensity line at 39.1 ± 2.0 Å d-spacing and weak lines at 22.4 ± 1.0 and 19.4 ± 1.0 Å. TEM indicated that this product contained the ultra-large pore material.

Example 14

A mixture of 125 grams of 29% CTMA chloride aqueous solution, 200 grams of water, 3 grams of sodium aluminate (in 50 grams H_2O), 65 grams of Ultrasil, amorphous precipitated silica available from PQ Corporation, and 21 grams NaOH (in 50 grams H_2O) was

stirred thoroughly and crystallized at 150°C for 168 hours. The reaction mixture had the following relative molar composition in terms of moles per mole silica:

5 0.10 moles (CTMA)₂O
 21.89 moles H₂O
 0.036 moles NaAlO₂
 0.53 moles NaOH

10 The solid product was isolated by filtration, washed with water, dried for 16 hours at room temperature and calcined at 540°C for 10 hours in air. The calcined product proved to have a surface area of 840 m²/g, and the following equilibrium adsorption capacities in grams/100 grams:

15 H₂O 15.2
 Cyclohexane 42.0
 n-Hexane 26.5
 Benzene 62

20 The X-ray diffraction pattern of the calcined product may be characterized as including a very strong relative intensity line at 40.5 ± 2.0 Å d-spacing. TEM indicated that the product contained the ultra-large pore material.

Example 15

25 To make the primary template mixture for this example, 240 grams of water was added to a 92 gram solution of 50% dodecyltrimethylammonium hydroxide, 36% isopropyl alcohol and 14% water such that the mole ratio of Solvent/R_{2/f}O was 155. The mole ratio of H₂O/R_{2/f}O in this mixture was 149 and the IPA/R_{2/f}O mole ratio was 6. To the primary template mixture was
30 added 4.15 grams of sodium aluminate, 25 grams of HiSil, 100 grams of aqueous tetramethylammonium silicate solution (10% SiO₂) and 13.2 grams of 25% aqueous tetramethylammonium hydroxide solution. The

mole ratio of $R_{2/f}O/(SiO_2+Al_2O_3)$ was 0.28 for the mixture.

This mixture was stirred at 25°C for 1 hour. The resulting mixture was then placed in an autoclave at 100°C and stirred at 100 rpm for 24 hours. The mixture in the autoclave had the following relative molar composition in terms of moles per mole SiO_2 :

	0.05 mole Na_2O
	0.036 mole Al_2O_3
10	0.18 mole $(C_{12}TMA)_2O$
	0.12 mole $(TMA)_2O$
	36.0 moles H_2O
	1.0 mole IPA

The resulting solid product was recovered by filtration, washed with water and dried in air at ambient temperature. The product was then calcined at 540°C for 1 hour in nitrogen, followed by 6 hours in air.

The calcined product proved to have a surface area of 1223 m^2/g and the following equilibrium adsorption capacities in grams/100 grams:

	H_2O	25.5
	Cyclohexane	41.1
	n-Hexane	35.1
25	Benzene	51

The X-ray diffraction pattern of the calcined product may be characterized as including a very strong relative intensity line at 30.8 ± 1.5 Å d-spacing and weak lines at 17.9 ± 1.0 and 15.5 ± 1.0 Å. TEM indicated this product to contain the ultra-large pore material.

Example 16

A 50.75 gram quantity of decyltrimethylammonium hydroxide (prepared by contacting a ca. 29 wt. %

solution of decyltrimethylammonium bromide with a hydroxide-for-halide exchange resin) was combined with 8.75 grams of tetraethylorthosilicate. The mixture was stirred for 1 hour and then transferred to a polypropylene jar which was then placed in a steambox for 24 hours. The mixture had a composition in terms of moles per mole SiO_2 :

0.81 mole $(\text{C}_{10}\text{TMA})_2\text{O}$

47.6 moles H_2O

The resulting solid product was filtered and washed several times with warm (60-70°C) distilled water and with acetone. The final product was calcined to 538°C in N_2 /air mixture and then held in air for 8 hours. The calcined product proved to have a surface area of 915 m^2/g and an equilibrium benzene adsorption capacity of 35 grams/100 grams. Argon physisorption data indicated an argon uptake of 0.34 cc/gram, and a pore size of 15 Å.

The X-ray diffraction pattern of the calcined product of this example may be characterized as including a very strong relative intensity line at 27.5 ± 1.5 Å d-spacing and weak lines at 15.8 ± 1.0 and 13.7 ± 1.0 Å. TEM indicated that the product of this example contained the ultra-large pore material.

Example 17

To eighty grams of cetyltrimethylammonium hydroxide (CTMAOH) solution prepared as in Example 1 was added 1.65 grams of NaAlO_2 . The mixture was stirred at room temperature until the NaAlO_2 was dissolved. To this solution was added 40 grams of aqueous tetramethylammonium (TMA) silicate solution (10 wt.% SiO_2), 10 grams of HiSil, 200 grams of water and 70 grams of 1,3,5-trimethylbenzene (mesitylene). The resulting mixture was stirred at room temperature for

several minutes. The gel was then loaded into a 600 cc autoclave and heated at 105°C for sixty-eight hours with stirring at 150 rpm. The mixture had a composition in terms of moles per mole Al_2O_3 :

5 1.25 moles Na_2O
 27.8 moles SiO_2
 5.1 moles $(\text{CTMA})_2\text{O}$
 2.24 moles $(\text{TMA})_2\text{O}$
 2256 moles H_2O
10 80.53 moles 1,3,5-trimethylbenzene

The resulting product was filtered and washed several times with warm (60-70°C) distilled water and with acetone. The final product was calcined to 538°C in N_2 /air mixture and then held in air for 10 hours.

15 The calcined product proved to have an equilibrium benzene adsorption capacity of >25 grams/100 grams.

 The X-ray diffraction pattern of the calcined product may be characterized as including a broad, very strong relative intensity line at 102 Å d-spacing, but accurate positions of lines in the extreme low angle region of the X-ray diffraction pattern are very difficult to determine with conventional X-ray diffractometers. Furthermore, finer collimating slits were required to resolve a peak at this low 2-theta angle. The slits used in this example, starting at the X-ray tube, were 0.1, 0.3, 0.5 and 0.2 mm, respectively. TEM indicated that the product of this example contained several materials with different d_{100} values as observed in their electron diffraction patterns. These materials were found to possess d_{100} values between 85 Å d-spacing and 120 Å d-spacing.

20
25
30

Example 18

To eighty grams of cetyltrimethylammonium hydroxide (CTMAOH) solution prepared as in Example 1

was added 1.65 grams of NaAlO_2 . The mixture was stirred at room temperature until the NaAlO_2 was dissolved. To this solution was added 40 grams of aqueous tetramethylammonium (TMA) silicate solution (10 wt.% SiO_2), 10 grams of HiSil, 200 grams of water and 120 grams of 1,3,5-trimethylbenzene (mesitylene). The resulting mixture was stirred at room temperature for several minutes. The gel was then loaded into a 600 cc autoclave and heated at 105°C for ninety hours with stirring at 150 rpm. The mixture had a composition in terms of moles per mole Al_2O_3 :

1.25 moles Na_2O
27.8 moles SiO_2
5.1 moles $(\text{CTMA})_2\text{O}$
2.24 moles $(\text{TMA})_2\text{O}$
2256 moles H_2O
132.7 moles 1,3,5-trimethylbenzene

The resulting product was filtered and washed several times with warm ($60-70^\circ\text{C}$) distilled water and with acetone. The final product was calcined to 538°C in N_2 /air mixture and then held in air for 10 hours. The calcined product proved to have a surface area of $915 \text{ m}^2/\text{g}$ and an equilibrium benzene adsorption capacity of $>25 \text{ grams}/100 \text{ grams}$. Argon physisorption data indicated an argon uptake of $0.95 \text{ cc}/\text{gram}$, and a pore size centered on $78 \text{ \AA}$ (Dollimore-Heal Method, see Example 22(b)), but running from 70 to greater than 105 Angstroms. The X-ray diffraction pattern of the calcined product of this example may be characterized as having only enhanced scattered intensity in the very low angle region of the X-ray diffraction, where intensity from the transmitted incident X-ray beam is usually observed. However, TEM indicated that the product contained several materials with different d_{100}

values as observed in their electron diffraction patterns. These materials were found to possess d_{100} values between 85 Å d-spacing and 110 Å d-spacing.

Example 19

5 To eighty grams of cetyltrimethylammonium
hydroxide (CTMAOH) solution prepared as in Example 1
was added 1.65 grams of NaAlO_2 . The mixture was
stirred at room temperature until the NaAlO_2 was
dissolved. To this solution was added 40 grams of
10 aqueous tetramethylammonium (TMA) silicate solution (10
wt.% SiO_2), 10 grams of HiSil, and 18 grams of
1,3,5-trimethylbenzene (mesitylene). The resulting
mixture was stirred at room temperature for several
minutes. The gel was then loaded into a 300 cc
15 autoclave and heated at 105°C for four hours with
stirring at 150 rpm. The mixture had a composition in
terms of moles per mole Al_2O_3 :

1.25 moles Na_2O
27.8 moles SiO_2
20 5.1 moles $(\text{CTMA})_2\text{O}$
2.24 moles $(\text{TMA})_2\text{O}$
650 moles H_2O
19.9 moles 1,3,5-trimethylbenzene

The resulting product was filtered and washed
25 several times with warm (60-70°C) distilled water and
with acetone. The final product was calcined to 538°C
in N_2 /air mixture and then held in air for 8 hours.

The calcined product proved to have a surface area
of 975 m^2/g and an equilibrium benzene adsorption
30 capacity of >40 grams/100 grams. Argon physisorption
data indicated an argon uptake of 0.97 cc/gram, and a
pore size of 63 Å (Dollimore-Heal Method), with the
peak occurring at $P/P_0=0.65$.

The X-ray diffraction pattern of the calcined product of this example may be characterized as including a very strong relative intensity line at 63 ± 5 Å d-spacing and weak lines at 36.4 ± 2.0 , 31.3 ± 1.5 Å and 23.8 ± 1.0 Å d-spacing. TEM indicated that the product of this example contained the ultra-large pore material.

Example 20

Argon Physisorption Determination

To determine the pore diameters of the mesoporous products with pores up to 60 Å in diameter, 0.2 gram samples of the products of Examples 1 through 17 were placed in glass sample tubes and attached to a physisorption apparatus as described in U.S. Patent No. 4,762,010.

The samples were heated to 300°C for 3 hours in vacuo to remove adsorbed water. Thereafter, the samples were cooled to 87°K by immersion of the sample tubes in liquid argon. Metered amounts of gaseous argon were then admitted to the samples in stepwise manner as described in U.S. Patent No. 4,762,010, column 20. From the amount of argon admitted to the samples and the amount of argon left in the gas space above the samples, the amount of argon adsorbed can be calculated. For this calculation, the ideal gas law and the calibrated sample volumes were used. (See also S.J. Gregg et al., Adsorption, Surface Area and Porosity, 2nd ed., Academic Press, 1982). In each instance, a graph of the amount adsorbed versus the relative pressure above the sample, at equilibrium, constitutes the adsorption isotherm. It is common to use relative pressures which are obtained by forming the ratio of the equilibrium pressure and the vapor pressure P_0 of the adsorbate at the temperature where

the isotherm is measured. Sufficiently small amounts of argon were admitted in each step to generate 168 data points in the relative pressure range from 0 to 0.6. At least 100 points are required to define the isotherm with sufficient detail.

The step (inflection) in the isotherm, indicates filling of a pore system. The size of the step indicates the amount adsorbed, whereas the position of the step in terms of P/P_0 reflects the size of the pores in which the adsorption takes place. Larger pores are filled at higher P/P_0 . In order to better locate the position of the step in the isotherm, the derivative with respect to $\log(P/P_0)$ is formed. The adsorption peak (stated in terms of $\log(P/P_0)$) may be related to the physical pore diameter (λ) by the following formula:

$$\log(P/P_0) =$$

$$\log(P/P_0) = \frac{K}{d-0.38} \left[\frac{s^4}{3(L-D/2)^3} - \frac{s^{10}}{9(L-D/2)^9} - \frac{s^4}{3(D/2)^3} + \frac{s^{10}}{9(D/2)^9} \right]$$

where d = pore diameter in nanometers, $K = 32.17$, $S = 0.2446$, $L = d + 0.19$, and $D = 0.57$.

This formula is derived from the method of Horvath and Kawazoe (G. Horvath et al., J. Chem. Eng. Japan, 16 (6) 470(1983)). The constants required for the implementation of this formula were determined from a measured isotherm of ALPO-5 and its known pore size.

This method is particularly useful for microporous materials having pores of up to 60 Å in diameter.

5 The results of this procedure for the samples from Examples 1 through 16 are tabulated below. The samples from Examples 10, 13 and 15 gave two separate peaks, believed to be the result of two separate ultra-large pore phases in the products.

	<u>Examples</u>	<u>Pore Diameter, Å</u>
	1	32.2
10	2	35.4
	3	42.5
	4	39.6
	5	16.9
	6	27.3
15	7	36.6
	8	42.6
	9	28.3
	10	22.8, 30.8
	11	36.8
20	12	36.1
	13	35.0, 42.1
	14	40.0
	15	22.4, 30.4
	16	15.0

25 By way of comparison, a commercially prepared sample of zeolite USY (equilibrium benzene sorption capacity of 20.7 grams/100 grams, X-ray diffraction pattern with all the lines of zeolite Y and with the highest d-spacing at 14 Å) had a pore diameter of 8.3 Å
30 as determined by the above method.

The method of Horvath and Kawazoe for determining pore size from physisorption isotherms was intended to be applied to pore systems of up to 20 Å diameter; but

with some care as above detailed, its use can be extended to pores of up to 60 Å diameter.

In the pore regime above 60 Å diameter, the Kelvin equation can be applied. It is usually given as:

5

$$\ln(P/P_0) = \frac{-2\gamma V}{r_k RT} \cos \theta$$

where:

- 10
- γ = surface tension of sorbate
 - V = molar volume of sorbate
 - θ = contact angle (usually taken for practical reasons to be 0)
 - R = gas constant
 - T = absolute temperature
 - 15 r_k = capillary condensate (pore) radius
 - P/P_0 = relative pressure (taken from the physisorption isotherm)

The Kelvin equation treats adsorption in pore systems as a capillary condensation phenomenon and relates the pressure at which adsorption takes place to the pore diameter through the surface tension and contact angle of the adsorbate (in this case, argon). The principles upon which the Kelvin equation are based are valid for pores in the size range 50 to 1000 Angstrom diameter. Below this range the equation no longer reflects physical reality, since true capillary condensation cannot occur in smaller pores; above this range the logarithmic nature of the equation precludes obtaining sufficient accuracy for pore size determination.

20

25

30

The particular implementation of the Kelvin equation often chosen for measurement of pore size is that reported by Dollimore and Heal (D. Dollimore and G.R. Heal, J. Applied Chem, 14, 108 (1964)). This

method corrects for the effects of the surface layer of adsorbate on the pore wall, of which the Kelvin equation proper does not take account, and thus provides a more accurate measurement of pore diameter. While the method of Dollimore and Heal was derived for use on desorption isotherms, it can be applied equally well to adsorption isotherms by simply inverting the data set.

Transmission Electron Microscopy

In order to illuminate the microstructure of materials by transmission electromicroscopy (TEM), samples must be thin enough for an electron beam to pass through them, generally 500-1000 Å or so thick. The crystal morphology of the present materials usually required that they be prepared for study by ultramicrotomy. While time consuming, this technique of sample preparation is quite familiar to those skilled in the art of electron microscopy. The materials are embedded in a resin, in this case a commercially available low viscosity acrylic resin L.R. WHITE (hard), which is then cured at 80°C for 1 1/2 hours. Thin sections of the block are cut on an ultramicrotome using a diamond knife and sections in the thickness range 500-1000 Å are collected on fine mesh electron microscope support grids. For these materials, an LKB model microtome with a 45°C diamond knife edge was used; the support grids were 400 mesh copper grids. After evaporation of a thin carbon coating on the sample to prevent charging in the microscope (light gray color on a white sheet of paper next to the sample in the evaporator), the samples are ready for examination in the TEM.

High resolution TEM micrographs show projections of structure along the direction that the sample is

viewed. For this reason, it is necessary to have a sample in specific orientations to see certain details of the microstructure of the material. For crystalline materials, these orientations are most easily chosen by observing the electron diffraction pattern (EDP) that is produced simultaneously with the electron microscope image. Such EDPs are readily produced on modern TEM instruments using, e.g. the selected area field limiting aperture technique familiar to those skilled in the art of electron microscopy. When an EDP with the desired arrangement of diffraction spots is observed, the corresponding image of the crystal giving that EDP will reveal details of the microstructure along the direction of projection indicated by the EDP. In this way, different projections of a crystal's structure can be observed and identified using TEM.

In order to observe the salient features of the crystalline product, it is necessary to view the material in an orientation wherein the corresponding EDP gives a hexagonal arrangement of diffraction spots from a single individual crystal. If multiple crystals are present within the field limiting aperture, overlapping diffraction patterns will occur that can be quite difficult to interpret. The number of diffraction spots observed depends to a degree upon the regularity of the crystalline arrangement in the material, among other things. At the very least the inner ring of bright spots should be observed to obtain a good image. Individual crystals can be manipulated by specimen tilt adjustments on the TEM until this orientation is achieved. More often, it is easier to take advantage of the fact that the specimen contains many randomly oriented crystals and to simply search through the sample until a crystal giving the desired

EDP (and hence orientation) is located. This latter technique was used to produce the electron micrographs.

5 Microtomed samples of materials from the Examples were examined by the techniques described above in a JEOL 200 CX transmission electron microscope operated at 200,000 volts with an effective 2 Å objective aperture in place. The instrument has a point-to-point resolution of 4.5 Å. Other experimental arrangements familiar to one skilled in the art of high resolution (phase contrast) TEM could be used to produce equivalent images provided care is taken to keep the objective lens on the underfocus (weak leans) side of the minimum contrast lens current setting.

10

Examples 21 - 24

15 The following examples demonstrate the lube hydrocracking process. These examples utilize the processing of a Statfjord heavy neutral distillate whose properties are given in Table 3 below, together with the properties of the oil after solvent dewaxing to 0°F pour point (ASTM D-97 or equivalent such as Autopour). It can be seen that the feedstock has high nitrogen content of 1500 ppm and that the distillate VI after solvent dewaxing is 53. The objective of lube hydrocracking the distillate is to increase the VI level to the 95-100 VI range after solvent dewaxing while maximizing lube yield.

20

25

Table 3

Statfjord Heavy Neutral
Distillate Properties

	Hydrogen, wt.%	12.83
5	Nitrogen, ppm	1500
	Basic Nitrogen, ppm	466
	Sulfur, wt.%	0.72
	API Gravity	22.0
	KV @ 100°C, mm ² /s	18.52
10	Composition, wt.%	
	Paraffins	18.3
	Naphthenes	32.2
	Aromatics	49.5
	Sim Dist, wt.%	
15	IBP	765
	5	846
	10	880
	95	1086

Solvent Dewaxed Oil Properties

20	KV @ 100°C, mm ² /s	20.1
	VI	53
	Pour Point,	
	°C (°F)	-18 (0)
	Lube Yield, wt.%	87

25 Example 21

This Example provides a comparison with a zeolite catalyst (NiW/USY).

30 The heavy neutral distillate feed was processed over a fixed bed reactor containing a NiW/USY hydrocracking catalyst made by the following procedure: a commercial USY (PQ Corp. Z-14 USY) was combined with Al₂O₃ to form a mixture of 65 parts, by weight, zeolite and 35 parts alumina. Water was added to this mixture to allow the resulting catalyst to be formed into

extrudates. The catalyst was then thermally treated at 1000°F in flowing air for three hours. A portion of the resultant extrudate was exchanged with aqueous solutions of ammonium nitrate and was subsequently dried overnight at 121°C (250°F). Following a three hour 538°C (1000°F) air calcination, 100% steam was introduced and the temperature maintained at 538°C (1000°F) for 10 hours. Nickel and tungsten were incorporated via incipient wetness coimpregnation using solutions of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $(\text{NH}_4)_6\text{H}_2\text{W}_{12}\text{O}_{40} \cdot \text{H}_2\text{O}$. After drying, the extrudates were calcined for three hours in flowing air at 538°C (1000°F). The Ni and W loadings on the final catalyst were 5.8 and 16.6 wt.%, respectively.

The processing conditions were 10450-18720 kPa (1500-2700 psig) hydrogen pressure, 1335 m.l.l.^{-1} (7500 SCFB) hydrogen circulation and 0.5 to 1.0 LHSV. The total liquid product of the reactor was distilled to a nominal 343°C (650°F+) cut-point and the feed was subsequently dewaxed with a 60/40 mixture of MEK/toluene. The results of these experiments are summarized in Table 4 below.

Table 4
(LHDC with NiW/USY)

	Temp., °C (°F)	371 (700)	385 (725)	399 (750)
	Pressure,			
5	kPa (psig)	18720 (2700)	18729 (2700)	10446 (1500)
	LHSV	0.5	0.5	1.0
	343°C (650°F+)			
	conv., wt.%	15.2	29.3	20.0
	Lube Properties			
10	KV @ 100°C, mm ² /s	14.7	10.95	10.68
	SUS @ 38°C (100°F)	982	519	515
	VI	72	94	90
	Pour Point, °C (°F)	-15 (5)	-15 (5)	-15 (5)
	Lube Yield, wt.%	80.9	60.1	63.5

15 Example 22

20 This example illustrates the use of a commercially available amorphous catalyst (NiW/Al₂O₃) without any promoter. Conditions for this example were 13890 kPa (2000 psig) hydrogen pressure, 517 n.l.l.⁻¹ (7500 SCFB) hydrogen circulation, and 0.5 LHSV. Table 5 below summarizes results of this experimental run.

Table 5
(LHDC With Unfluorided NiW/alumina)

	Temp., °C (°F)	399 (750)	399 (765)	399 (775)
	Pressure,			
5	kPa (psig)	13890 (2000)	13890 (2000)	13890 (2000)
	LHSV	0.5	0.5	0.5
	343°C+ (650°F+)			
	conv., wt.%	15.5	21.5	28.2
	Lube Properties			
10	KV @ 100°C, mm ² /s	11.44	9.83	8.86
	SUS @ 38°C (100°F)	602	449	369
	VI	83.9	91.7	97.0
	Pour Point,			
	°C (°F)	-21(-5)	-21(-5)	-23 (-10)
15	Lube Yield, wt.%	70.2	64.3	58.6

Example 23

This example utilizes the same catalyst as Example 22 except that the catalyst is activated by in-situ fluoriding in the fixed bed reactor to achieve a target 4-7 wt.% flourine on catalyst. This was accomplished by flouriding the catalyst with a high level (600 ppm) of flourine in the distillate for a one week period after which the flourine level is reduced to a 25 ppm level at which it is held for the remainder of the experimental run. O-fluorotoluene was used as the fluoriding agent. Processing conditions were 13890 kPa (2000 psig) hydrogen, 1335 n.l.l.⁻¹ (7500 SCFB) hydrogen circulation and 0.5 to 1.0 LHSV. The data from these experimental runs are given in Table 6 below.

Table 6
(LHDC With Fluorided NiW/alumina)

	Temp., °C (°F)	407 (764)	399 (751)	413 (775)
	Pressure,			
5	kPa (psig)	13890 (2000)	13890 (2000)	13890 (2000)
	LHSV	1.0	0.5	1.0
	343°C+ (650°F+)			
	conv., wt.%	16.3	18.9	21.7
	Lube Properties			
10	KV @ 100°C, mm ² /s	10.22	9.25	9.12
	SUS @ 38°C (100°F)	468	392	380
	VI	93.8	97.5	98.8
	Pour Point, °C (°F)	-1 (30)	-7 (20)	-7 (20)
	Lube Yield, wt.%	74.4	70.0	68.5

15 Example 24

This example shows the benefits of using an M41S molecular sieve for selective lube hydrocracking. A NiW/MCM-41 catalyst was prepared as outlined below.

20 A sample of MCM-41 (40 Å) was prepared in accordance with the following method.

The following mixture was charged to an autoclave:

9965g Cetyltrimethylammonium (CTMA) hydroxide,
prepared by contacting a 29wt.%
N,N,N-trimethyl-hexadecylammonium
25 chloride solution with a
hydroxide-for-halide exchange resin,
208g Sodium aluminate,
492g Tetramethylammonium silicate (10% aqueous
solution),
30 1245g Precipitated hydrated silica (Hisil +).

The mixture was crystallized at 100°C for 20 hrs. with stirring under autogeneous pressure. The resulting product was recovered by filtration and dried

in air at ambient temperature. A sample of the product was calcined at 540°C for 1 hour in nitrogen, followed by 6 hours in air for characterization.

5 The calcined product had a surface area of 1120 m²/g and the following equilibrium absorption capacities in grams/100 grams:

	H ₂ O	10.8
	Cyclohexane	>50
	n-hexane	>50
10	Benzene	67

The calcined product exhibited very strong relative intensity line at 38.4 + 2.0 Å d-spacing, and weak lines at 22.6 + 1.0, 20.0 + 1.0, and 15.2 + 1.0 Å.

15 The MCM-41 product was exchanged with room temperature aqueous solutions of ammonium nitrate and subsequently dried overnight at 121°C (250°F). A portion of the resultant crystals was combined with Al₂O₃ to form a mixture of 65 parts, by weight MCM-41 and 35 parts alumina. Water was added to this mixture
20 to allow the resulting catalyst to be formed into extrudates. The catalyst was activated by calcination at 510°C (950°F) in 5v/v/min of nitrogen for 6 hours followed by the replacement of the nitrogen with 5v/v/min of air. The calcination was completed by
25 raising the temperature to 1000°F and maintaining that temperature in 5v/v/min air for 18 hours. Nickel and tungsten were incorporated via incipient wetness coimpregnation using solutions of Ni(NO₃)₂·6H₂O and (NH₄)₆H₂W₁₂₀·40H₂O. After drying overnight at 121°C
30 (250°F), the extrudate was calcined in 5v/v/min air at 538°C (1000°F) for 3 hours. Physical and chemical

properties of the NiW/MCM-41/Al₂O₃ catalyst are:

	Nickel, wt.%	3.7
	Tungsten, wt.%	9.2
	Sodium, ppm	200
5	Surface Area, m ² /g	530
	Pore Volume, ml/g	0.780
	Particle Density, g/ml	0.883
	Real Density, g/ml	2.837

This catalyst was used to hydrocrack the
 10 distillate at temperatures from 385 to 701°C (725 to
 754°F), 13890 kPa (2000 psig) hydrogen pressure, 1335
 n.l.l.⁻¹ (7500 SCFB) hydrogen circulation and 0.55 to
 0.61 LHSV. The data from these experimental runs are
 summarized in Table 7 below:

15	Table 7 (LHDC with NiW/MCM-41)			
	Temp., °C (°F)	385 (725)	393 (739)	401 (754)
	Pressure,			
	kPa (psig)	13890 (2000)	13890 (2000)	13890 (2000)
20	LHSV	0.61	0.54	0.55
	343°C (650°F+)			
	conv., wt.%	9.3	20.8	36.0
	Lube Properties			
	KV @ 100°C, mm ² /s	13.08	10.46	7.59
25	SUS @ 38°C (100°F)	772	468	261
	VI	79	98.1	113.3
	Pour Point,			
	°C (°F)	-9 (15)	-1 (30)	-1 (30)
	Lube Yield, wt.%	80.5	66.6	54.3

30 The NiW/MCM-41 catalyst was selective for
 upgrading the heavy neutral distillate from a raw
 distillate VI of 53 to a 98 VI product at a conversion

level of 20.8 wt.%. The lube yield versus VI selectivity data for all the examples is represented in Figure 1. It can be seen that the unfluorided NiW/MCM-41 catalyst produces a higher VI product at a given lube yield or alternatively a higher lube yield at a given VI compared to the other unfluorided catalysts evaluated, i.e. NiW/USY or NiW/alumina. In the VI range of commercial significance (95-100 VI), the fluorided NiW/alumina catalyst has a slightly higher lube yield vs. VI selectivity compared to the NiW/MCM-41 catalyst but has the draw-back of requiring fluorine. Additionally, the activity of the NiW/MCM-41 catalyst as determined by the temperature requirement to achieve target conversion was very favorable compared to both the fluorided and unfluorided NiW/alumina catalysts. This is shown in Table 8 below where a nominal 20 wt.% 343°C+ (650°F+) conversion severity was achieved.

Table 8

	<u>Catalyst activity</u>		
	<u>Unfluorided</u> <u>NiW/MCM-41</u>	<u>Fluorided</u> <u>NiW/alumina</u>	<u>NiW/alumina</u>
Temp., °C (°F)	393 (739)	407 (765)	399 (751)
343°C+ (650°F+)			
conv. wt.%	20.8	21.5	18.9
Pressure,			
kPa (psig)	13890 (2000)	13890 (2000)	13890 (2000)
LHSV	0.54	0.5	0.5

The NiW/MCM-41 catalyst was more active than both the fluorided and unfluorided NiW/alumina catalysts. Since lube hydrocracker catalysts typically age with time on-stream, the increased activity of the MCM-41

catalyst system is beneficial in terms of the potential for improvements in commercial cycle length.

Examples 25 - 29

5 The following examples demonstrate the wax hydrocracking/hydroisomerization process using a heavy neutral wax feed.

Example 25 This example provides a comparison with an amorphous catalyst. The feed was a heavy neutral (HN) slack wax whose properties are listed in Table 9 below.

Table 9
Properties of Heavy Neutral Slack Wax

	Hydrogen, wt.%	14.56
	Nitrogen, ppm	54
5	Sulfur, wt.%	0.102
	API Gravity	34.9
	KV @ 100°C, mm ² /s	7.117
	Solvent Extractables, wt.% (D3235)	34.05
	Simulated Distillation, °C (°F)	
10	IBP/5	391/429 (736/805)
	10/20	442/459 (828/858)
	30/40	471/481 (879/898)
	50/60	491/502 (916/936)
	70/80	514/528 (957/982)
15	90/EP	546/591 (1014/1095)
	<u>Dewaxed Oil Properties</u>	
	Nitrogen, ppm	95
	Sulfur, wt.%	0.220
	Pour point, C° (°F)	-18 (0)
20	KV @ 40°C, mm ² /s	92.04
	KV @ 100°C, mm ² /s	10.53
	VI	96.2
	Composition, wt.%	
	Paraffins	23.2
25	Mononaphthenes	19.4
	Polynaphthenes	37.1
	Aromatics	20.3

30 The feed was processed over a fixed bed reactor containing NiW/alumina fluorided catalyst that was sulfided and then fluorided in-situ by adding 600 ppm of fluorine as orthofluorotoluene in the slack wax feed for approximately one week to target a fluorine level of 2-4 wt.% on catalyst. The operating conditions for

5 the run were 2000 psig hydrogen pressure 1 LHSV and the reactor temperature was varied from 374° to 402°C (705° to 755°F) to cover a wide conversion range. The total liquid product from the hydrocracking step was then distilled to a nominal 343°C+ (650°F+) cut-point. The bottoms fraction was then solvent dewaxed to a target -18°C+ (0°F) pour point. The results of these runs are summarized in Table 10 below.

Table 10

Wax Hydrocracking - NiW/Al₂O₃ Catalyst

Mass Bal. No.	411	412	413	415	416	417	418
Reactor temp,							
C° (°F)	393 (740)	399 (750)	402 (755)	391 (735)	385 (725)	379 (715)	374 (705)
343°C- (650°F-)							
Conv, wt. %	28	40	48	23	17	10	9
Lube Properties							
KV @ 100°C	5.0	4.3	4.0	5.1	5.4	5.9	6.7
VI	137	143	140	146	141	137	131
Pour Point,							
°C (°F)	-15 (5)	-18 (0)	-21 (-5)	-18 (0)	-21 (-5)	-15 (5)	-9 (15)
VI @ -18°C (0°F)							
Pour	136	143	141	146	142	136	128
Lube Yield, wt. %	40	43	42	40	34	33	29
Wax Conversion	50	74	84	42	24	12	4

Boiling point conversion is defined as:

$$650^{\circ}\text{F- conversion} = \frac{650^{\circ}\text{F+ in Feed}}{650^{\circ}\text{F+ in Feed} - 650^{\circ}\text{F+ in Product}}$$

20 Wax Conversion is defined as:

$$\text{Wax Conversion} = \frac{\text{Wt\% Wax in Feed}}{\text{Wt\% Wax in Feed} - \frac{\text{Wt\% Unconverted Wax}}{\text{after Solvent Dewaxing}}}$$

Example 26

This example illustrates the use of the ultra-large pore size catalysts.

A NiW/MCM-41 catalyst was prepared as described below.

A sample of MCM-41 (40 Å) was prepared by crystallizing the following mixture (parts by weight) in an autoclave:

48 parts Cetyltrimethylammonium (CTMA) hydroxide,
prepared by contacting a 29 wt.% N,N,N-trimethyl-1-hexadecylammonium chloride solution with a hydroxide-for-halide exchange resin, 1,
1 part Sodium aluminate,
24 parts Tetramethylammonium silicate (10% aqueous solution),
6 parts Precipitated hydrated silica (Hisil, ♦).

The mixture was crystallized at 100°C for 24 hours with stirring under autogeneous pressure. The resulting product was recovered by filtration and dried in air at ambient temperature. A sample of the product was calcined at 540°C for 1 hour in nitrogen, followed by 6 hours in air. The characteristics of the product were consistent with its identity as MCM-41.

The MCM-41 was exchanged with room temperature aqueous solutions of ammonium nitrate and subsequently dried overnight at 121°C (250°F). A portion of the resultant crystals was combined with Al_2O_3 to form a mixture of 65 parts, by weight MCM-41 and 35 parts alumina. Water was added to this mixture to allow the resulting catalyst to be formed into extrudates. The catalyst was activated by calcination at 510°C (950°F) in 5v/v/min of nitrogen for 6 hours followed by the

5 replacement of the nitrogen with 5v/v/min of air. The calcination was completed by raising the temperature to 538°C (1000°F) and maintaining that temperature in 5v/v/min air for 18 hours. Nickel and tungsten were incorporated by incipient wetness coimpregnation using solutions of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $(\text{NH}_4)_6\text{H}_2\text{W}_{12}\text{O}_{40} \cdot 40\text{H}_2\text{O}$. After drying for 12 hours at 121°C (250°F), the extrudate was calcined in 5v/v/min air at 538°C (1000°F) for 3 hours.

10 The physical and chemical properties of the NiW/MCM-41/Al₂O₃ catalyst are set out below:

	Nickel, wt.%	5.8
	Tungsten, wt.%	29.1
	Sodium, ppm	200
15	Surface Area, m ² /g	242
	Packing Density, g/cc	0.749

This catalyst was used for wax hydrocracking/hydroisomerization at the following process conditions: 13890 kPa abs. (2000 psig) hydrogen pressure, 1335 n.l.l.⁻¹ (7500 SCF/Bbl) hydrogen circulation and 1 LHSV, as in Example 21, using the same wax feed as in Example 21. The operating temperature was adjusted from 382° to 397°C (720° to 746°F) to span a range of 343°C (650°F-) boiling point conversions. Product work-up was the same as in Example 21, that is, by distillation to a 343°C+ (650°F+) cutpoint followed by solvent dewaxing to a -18°C (0°F) pour point. The results of these runs are given in Table 11.

Table 11

Max HDC/HDI

	Mass Bal. No.	82	84	85	86	87	88	90	92
5	Reactor temp, °C (°F) 343°C- (650°F-) Conv, wt. %	382(720) 18.4	385(725) 21.5	385(725) 23.6	389(733) 29.2	389(732) 29.8	393(740) 41.1	397(746) 59.5	388(731) 35.6
10	Inbe Properties: KV @ 100° VI Pour Point, °C (°F) VI @ -18°C (0°F) Pour Pt	5.81 143.6 -7 (20) 139.6	5.47 145.7 -15 (5) 144.7	5.30 144.3 -15 (5) 143.3	4.86 142.8 -15 (5) 141.8	4.857 145.7 -15 (5) 144.7	4.55 142.0 -12 (10) 140	4.29 141.3 -12 (10) 139.3	5.02 145.6 -15 (5) 144.6
15	Inbe Yield, wt. % Wax Conversion	39.5 42.3	38.6 49.6	40.3 42.7	47.6 65.4	44.3 68.7	47.5 81.3	43.9 84.7	47.2 65.6

Figure 2 of the drawings shows that the activity of the NiW/MCM-41 is higher than the activity of the fluorided NiW/alumina catalyst. For example, at 30 wt.% 343°C- (650°F-) conversion, the fluorided catalyst
5 required a 394°C (742°F) reactor temperature, whereas, the MCM-41 catalyst required 5.6°C (10°F) lower temperature of 389°C (732°F). In the preferred boiling point conversion range of 30-60 wt.% 343°C- (650°F-) conversion or greater, this activity advantage is
10 beneficial in terms of lower start-of-cycle temperature and potentially longer catalyst life.

Figure 3 shows that the lube yield for the fluorided NiW/alumina and the NiW/MCM-41 catalysts are similar at low wax conversions below 50 wt.%, but at
15 higher wax conversion the unpromoted NiW/MCM-41 catalyst has a desirable yield number benefit compared to the fluorided NiW/alumina catalyst.

Figure 4 shows that the lube VI of the NiW/MCM-41 is comparable to the VI obtained with the fluorided
20 NiW/alumina catalyst.

Figure 5 shows a viscosity benefit of the MCM-41 products. At a given wax conversion the lubes obtained from the MCM-41 based catalyst are higher in viscosity than the fluorided amorphous catalyst. Since the wax
25 hydrocracking/hydroisomerization process significantly reduces the viscosity of the hydrocracked/hydroisomerized feed, it is desirable to maintain viscosity as high as possible. For example, the target viscosity for this feed is 5 mm²/s at 100°C; the
30 fluorided alumina catalyst can achieve this at 50 wt.% wax conversion. The MCM-41 can operate at much higher wax conversion of 65 wt.% and still achieve target viscosity. There are significant commercial benefits

to operating at higher wax conversion, such as, reduction in MEK loading with higher wax conversion and reduction in size of the unconverted wax recycle stream.

- 5 A hydrotreating reactor may be provided downstream of the hydroisomerization reactor to further stabilize the lube product.



CLAIMS:

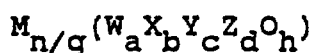
1. A process for producing lubricant products which comprises hydrocracking a feedstock comprising a high boiling hydrocarbon feed in the presence of hydrogen with a bifunctional hydrocracking catalyst having acidic functionality and
5 hydrogenation-dehydrogenation functionality, and comprising an inorganic, non-layered, porous, crystalline phase material having pores with diameters of at least 13 Å and exhibiting, after calcination, an
10 X-ray diffraction pattern with at least one peak with a relative intensity of 100 at a d-spacing greater than 18 Å to produce a lube boiling range product.

2. A process according to Claim 1 in which the crystalline phase material has, after calcination, a hexagonal arrangement of uniformly-sized pores with diameters of at least 13 Å and exhibits a hexagonal
5 electron diffraction pattern that can be indexed with a d_{100} value greater than 18 Å.

3. A process according to Claim 1 in which the crystalline phase has an X-ray diffraction pattern following calcination with at least one peak whose d-spacing corresponds to the d_{100} value from the
5 electron diffraction pattern.

4. A process according to Claim 1 in which the crystalline phase exhibits a benzene adsorption capacity of greater than 15 grams benzene per 100 grams at 6.7 kPa (50 Torr) and 25°C.

5. A process according to Claim 1 in which the crystalline phase has a composition expressed as follows:





wherein M is one or more ions; n is the charge of the composition excluding M expressed as oxides; q is the weighted molar average valence of M; n/q is the number of moles or mole fraction of M; W is one or more
5 divalent elements; X is one or more trivalent elements; Y is one or more tetravalent elements; Z is one or more pentavalent elements; a, b, c, and d are mole fractions of W, X, Y, and Z, respectively; h is a number of from 1 to 2.5; and $(a+b+c+d) = 1$.

6. A process according to Claim 4 wherein W comprises a divalent first row transition metal or magnesium; X comprises aluminum, boron, gallium or iron; Y comprises silicon or germanium; and Z comprises
5 phosphorus.

7. A process according to Claim 4 wherein a and d are 0 and $h = 2$.

8. A process according to claim 7 wherein X comprises aluminum, boron, gallium or iron and Y comprises silicon or germanium.

9. A process according to Claim 1 in which the catalyst comprises at least one metal of Groups VIA, VIIA or VIIIA of the Periodic Table.

10. A process according to Claim 1 in which the catalyst comprises at least one metal of Group VIA and at least one metal of Group VIIIA of the Periodic Table.

11. A process according to Claim 1 in which the feed is contacted with the catalyst at a pressure of from 8,400 to 30,000 kPa (hydrogen partial pressure, reactor inlet), a temperature from 288° to 441°C, and a
5 space velocity from 0.2 to 2.0 LHSV.

12. A process according to Claim 11 in which the feed is contacted with the catalyst at a pressure of



from 10,000 to 18,000 kPa (hydrogen partial pressure, reactor inlet), a temperature from 343° to 427°C, and a space velocity from 0.5 to 2.0 LHSV.

13. A process according to Claim 1 in which the hydrocracking is carried out in the absence of any promoter which increases the acid acidity of the catalyst.

14. A process according to Claim 1 in which the hydrocracking is carried out in the absence of fluorine or any fluorine compound promoter.

15. A process according to Claim 1 in which the hydrocarbon feed comprises a distillate feed having an initial boiling point of at least 343°C (650°F).

16. A process according to Claim 15 in which the feed comprises a gas oil produced by the distillation of petroleum.

17. A process according to Claim 1 in which the hydrocracked product has a viscosity index of at least 90.

18. A process according to Claim 1 in which the hydrocracked product has a viscosity index from 95 to 140.

19. A process according to Claim 1 in which the hydrocracked product is dewaxed.

20. A process according to any one of Claims 1 to 14 wherein the feedstock comprises a petroleum wax feed which is subjected to hydrocracking and hydroisomerization.

21. A process according to Claim 20 in which the feed is contacted with the catalyst at a pressure of from 7000 to 20800 kPa (1,000 to 3,000 psig) (hydrogen partial pressure, reactor inlet), a temperature from



288° to 441°C (550° to 825°F), and a space velocity from 0.2 to 4.0 LHSV.

5 22. A process according to Claim 21 in which the feed is contacted with the catalyst at a pressure of from 10101 to 18030 kPa (1,450 to 2,600 psig) (hydrogen partial pressure, reactor inlet), a temperature from 343° to 427°C (650° to 800°F), and a space velocity from 0.5 to 2.0 LHSV.

23. A process according to Claim 21 in which the hydrocarbon feed comprises a petroleum wax having a wax content of at least 50 wt.%.

24. A process according to Claim 23 in which the feed comprises a slack wax having an oil content of from 20 to 40 wt.%.

25. A process according to Claim 20 in which the hydrocracked product has a viscosity index of at least 135.

26. A process according to Claim 20 in which the hydrocracked product has a viscosity index from 140 to 147.

27. A process according to Claim 20 in which the hydrocracked/ hydroisomerized product is dewaxed.

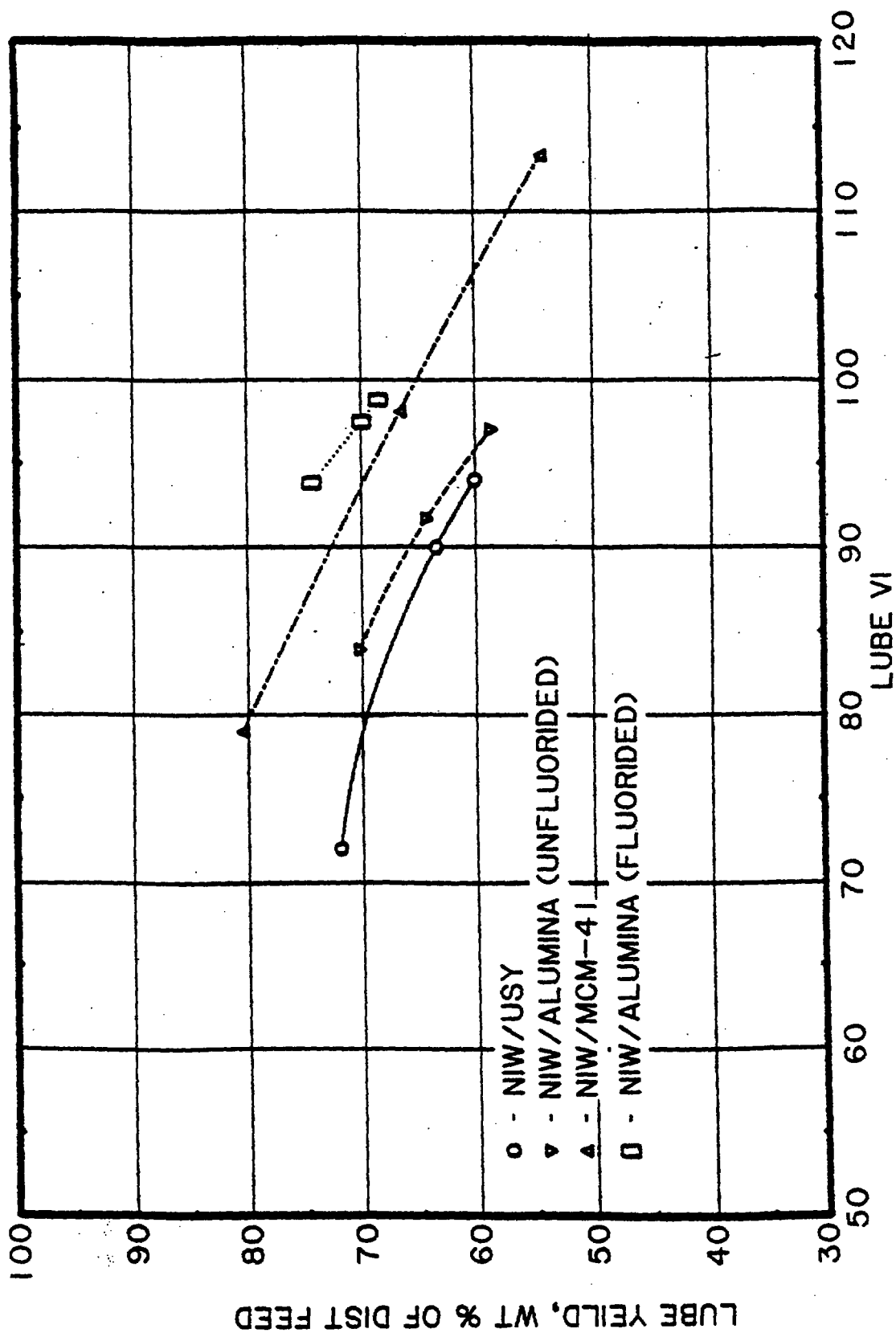


FIG. 1

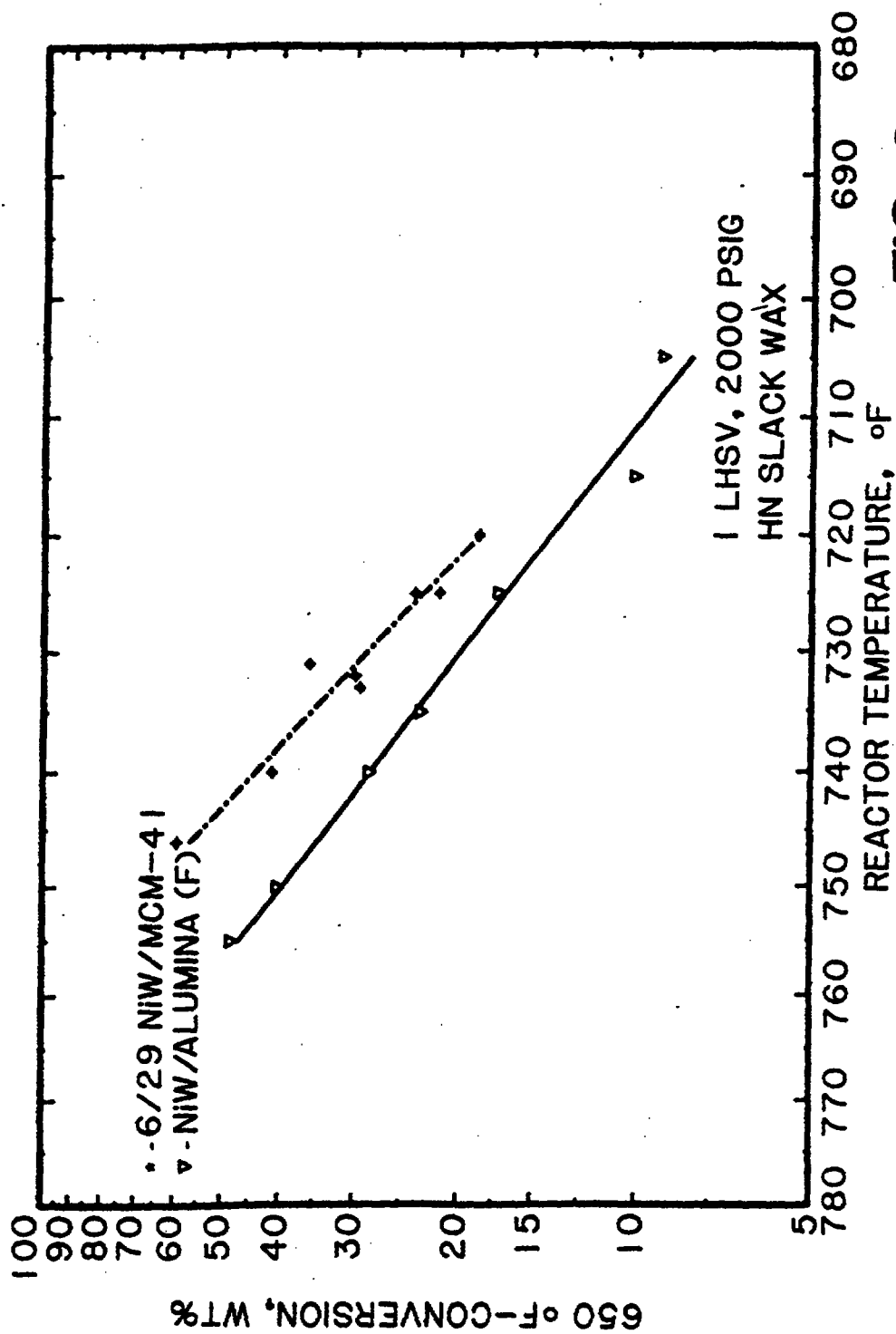


FIG. 2

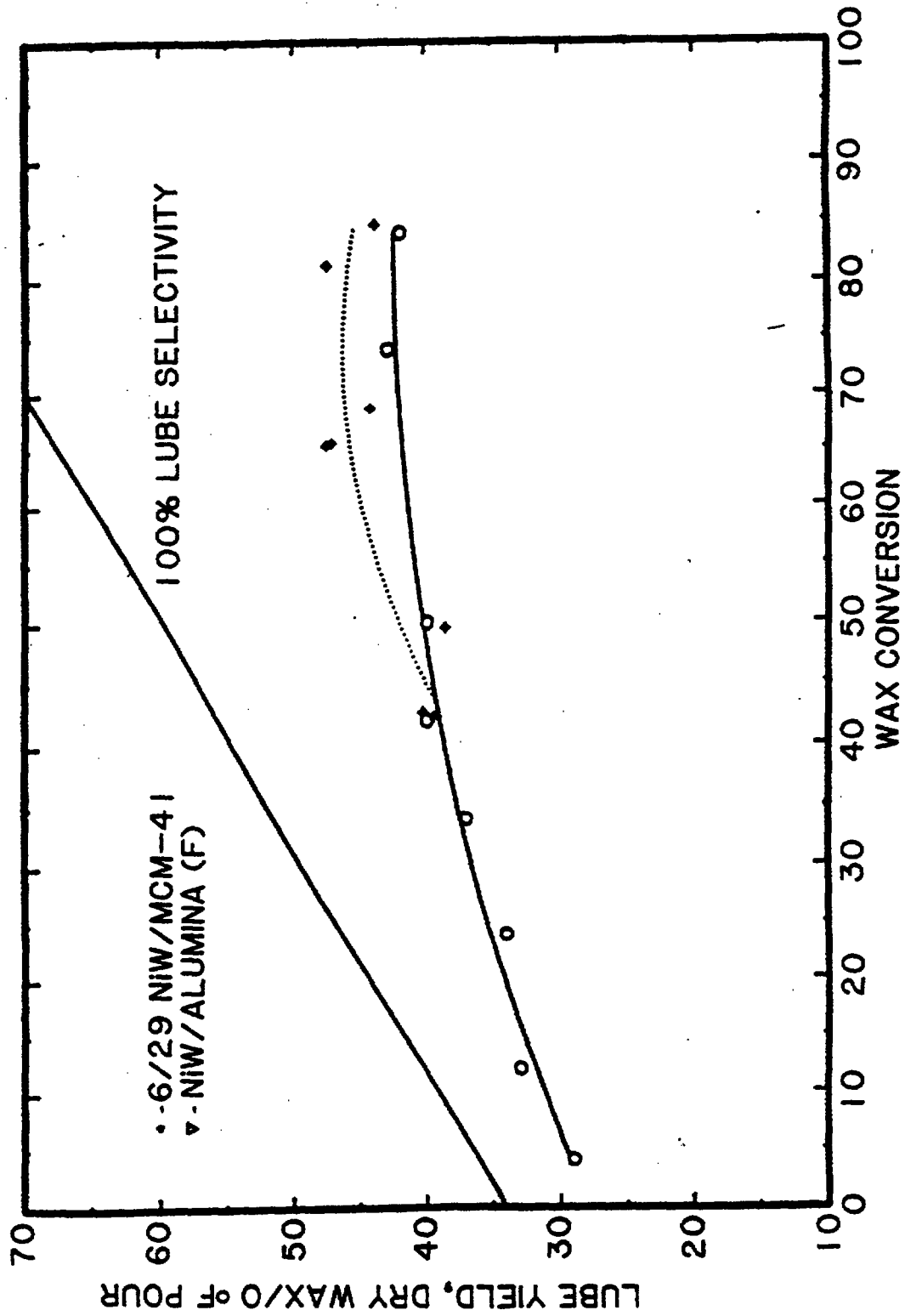


FIG. 3

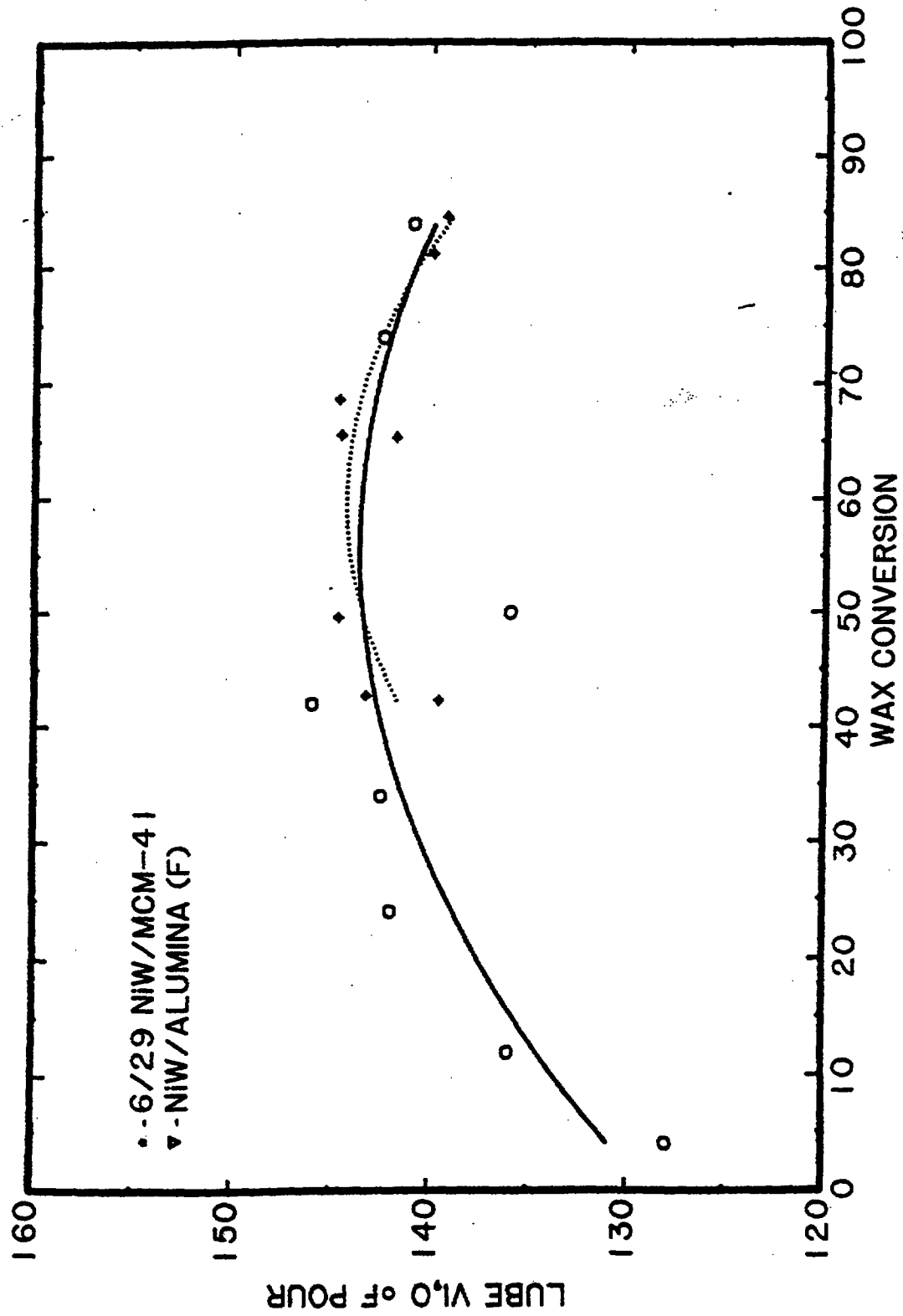


FIG. 4

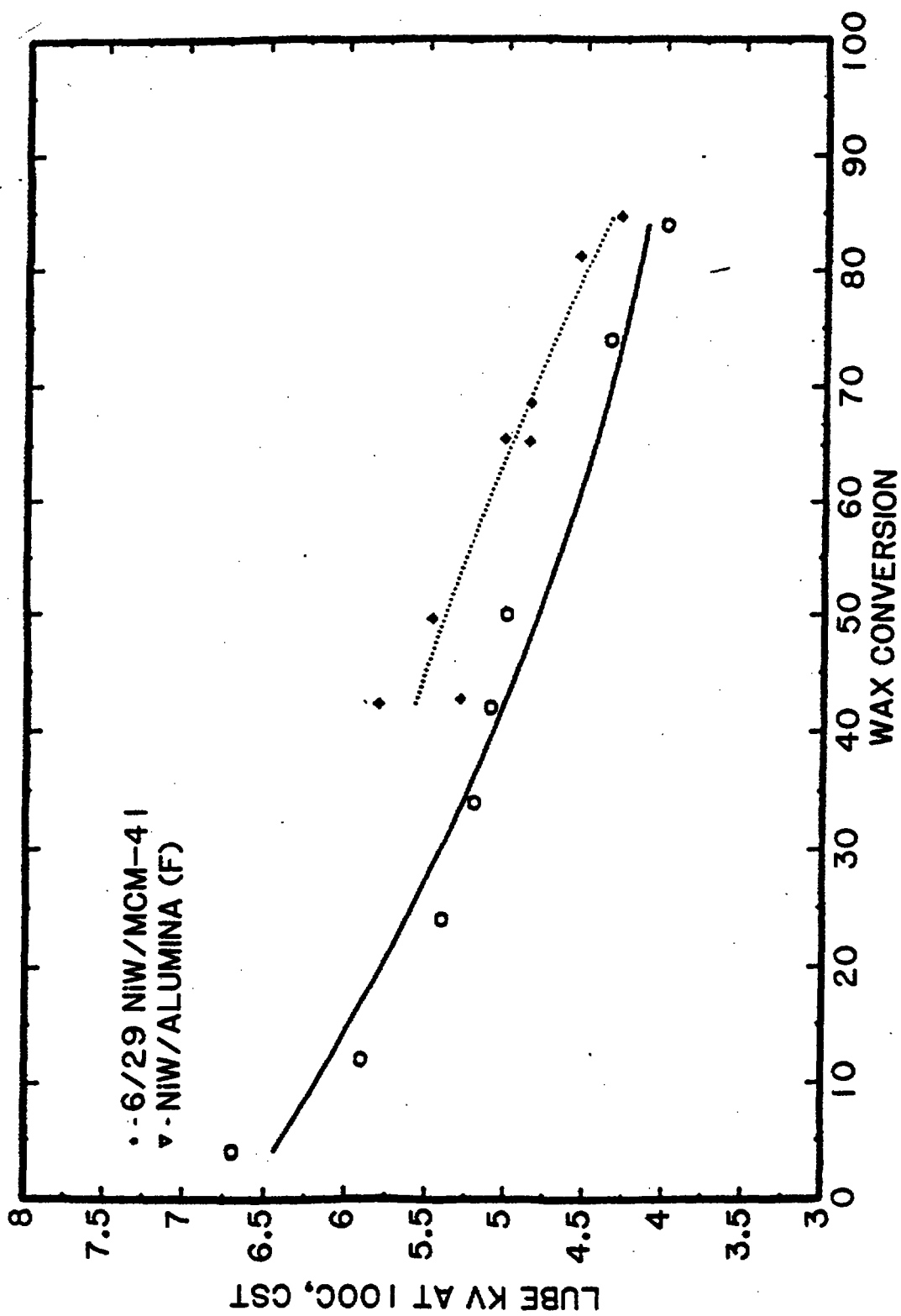


FIG. 5