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(54) **Title:** DEWAXING PROCESS USING ZEOLITES MTT AND GON

(57) **Abstract:** The present invention relates to the use of a combination of zeolites having the MTT and GON framework topologies defined by the connectivity of their tetrahedral atoms as a catalyst in a process for dewaxing hydrocarbon feedstocks.

DEWAXING PROCESS USING ZEOLITES MTT AND GON

BACKGROUND OF THE INVENTION

This application claims the benefit of U.S. Provisional Application Serial No. 60/706,134 filed August 4, 20005.

Field of the Invention

The present invention relates to processes for dewaxing hydrocarbon feedstocks employing a combination of zeolites MTT and GON as a catalyst.

State of the Art

Because of their unique sieving characteristics, as well as their catalytic properties, crystalline molecular sieves and zeolites are especially useful in applications such as hydrocarbon conversion, including dewaxing of hydrocarbon feedstocks. Zeolites may also be used for reducing the haze point in feedstocks such as bright stock. (See, for example, U.S. Patent No. 6,051,129, issued April 18, 2000 to Harris et al., in which zeolite EU-1 in combination with ZSM-48 and/or SSZ-32 is used to reduce haze in bright stock. This patent is incorporated by reference herein in its entirety.) Although many different crystalline molecular sieves have been disclosed, there is a continuing need for new zeolites with desirable properties for hydrocarbon and chemical conversions, and other applications.

SUMMARY OF THE INVENTION

In accordance with the present invention, there is provided a dewaxing process comprising contacting a hydrocarbon feedstock under dewaxing conditions with a catalyst comprising a combination of zeolites having the MTT and GON framework topologies defined by the connectivity of their

tetrahedral atoms (referred to herein simply as MTT and GON). The MTT and GON zeolites are preferably predominantly in the hydrogen form.

The present invention also includes a process for improving the viscosity index of a dewaxed product of waxy hydrocarbon feeds comprising contacting the waxy hydrocarbon feed under isomerization dewaxing conditions with a catalyst comprising a combination of zeolites MTT and GON, preferably predominantly in the hydrogen form.

The present invention further includes a process for producing a C_{20+} lube oil from a C_{20+} olefin feed comprising isomerizing said olefin feed under isomerization conditions over a catalyst comprising at least one Group VIII metal and a combination of zeolites MTT and GON. The zeolites may be predominantly in the hydrogen form.

In accordance with this invention, there is also provided a process for catalytically dewaxing a hydrocarbon oil feedstock boiling above about 350°F and containing straight chain and slightly branched chain hydrocarbons comprising contacting said hydrocarbon oil feedstock in the presence of added hydrogen gas at a hydrogen pressure of about 15-3000 psi with a catalyst comprising at least one Group VIII metal and a combination of zeolites MTT and GON, preferably predominantly in the hydrogen form.

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

The present invention also provides a process for reducing the cloud point of a hydrocarbon feed comprising contacting a hydrocarbon oil feedstock which has a major portion boiling over 1000ºF (538°C) with a catalyst system comprising a combination of a zeolite having MTT topology

and a zeolite having GON topology, wherein at least a portion of said feedstock is converted.

DETAILED DESCRIPTION OF THE INVENTION

In hydrodewaxing, one target is to hydroconvert the longest hydrocarbons in the feed. If these are left unconverted, they can cause haze in the product. The haze is quantified by cloud point.

The Gibbs free energy of adsorption for n-alkanes quantifies the ability of a particular zeolite structure for selectively absorbing and converting n-alkanes. In order to reduce the cloud point, it is advantageous to employ zeolites that impose a significantly lower Gibbs free energy of adsorption on a long as opposed to short n-alkane.

Gibbs free energies of adsorption can be determined with consistency and accuracy. Examples of these determinations are presented in "Journal of Physical Chemistry B" (2004), 108(33), 12301-12313. These determinations indicate that the difference between absorbing and converting a long n-alkane and a short n-alkane is only minimally different for MTT-type zeolites. The GON-type zeolites exhibit the maximum difference in Gibbs free energy of adsorption between long and short n-alkanes. It is surprising the Gibbs free energies of adsorption of these zeolites demonstrate such a markedly different response to the variation in n-alkane chain length. By employing GON-type zeolites in addition to MTT-type zeolites, the conversion of heavy wax (long n-alkanes) can be significantly increased, thereby lowering the cloud point of the product.

Zeolites having the MTT framework topology are known. For example, the zeolite designated "SSZ-32" and methods for making it are disclosed in U.S. Patent No. 5,053,373, issued October 1, 1991 to Zones. This patent discloses the preparation of zeolite SSZ-32 using an N-lower alkyl-N'-isopropylimidazolium cation as an organic structure directing agent (SDA),

sometimes called a templating agent. U.S. Patent No. 4,076,842, issued February 28, 1978 to Plank et al., discloses the preparation of the zeolite designated "ZSM-23", a zeolite with a structure similar to SSZ-32, using a cation derived from pyrrolidine as the SDA. Zeolites SSZ-32 and ZSM-23 are commonly referred to as having the MTT framework topology. Both of the aforementioned patents are incorporated herein by reference in their entirety. In addition, R. Szostak, Handbook of Molecular Sieves, 1992 lists zeolites designated ISI-4 and KZ-1 as having the MTT topology. The zeolite designated EU-13 is described in C. Baerlocher et al., Atlas of Zeolite Framework Types, 5th Revised Edition, 2001, International Zeolite Association as having the MTT topology.

Dewaxing processes using MTT zeolites are known. For example, U. S. Patent No. 4,222,855, issued September 16, 1980 to Pelrine et al., discloses a dewaxing process using ZSM-23 or ZSM-35. Likewise, U. S. Patent No. 5,376,260, issued December 27, 1994 to Santilli et al., discloses a dewaxing process using a catalyst containing SSZ-32. U. S. Patent No. 6,663,768, issued December 16, 2003 to Miller, also discloses a dewaxing process which uses ZSM-23 or SSZ-32 in the catalyst. U. S. Patent No. 4,601,993, issued July 22, 1986 to Chu et al., discloses a dewaxing process using a combination of ZSM-23 and zeolite Beta.

Zeolites having the GON topology are also known. For example, the zeolite designated “GUS-1” and a method of making it is disclosed in Plevert et al., “GUS-1: a mordenite-like molecular sieve with the 12-ring channel of ZSM-12”, Chem. Commun., 2000, pp. 2363-2364 which in incorporated herein by reference in its entirety. GON-type zeolites are 12 ring/8 ring zeolites with uni-dimensional channels.

The MTT and GON zeolites are used in the present invention in combination. As used herein, the term "combination" includes mixtures of the zeolites, layers of the zeolites, or any other configuration in which the feed comes in contact with both zeolites. For example, the combination may be a

graduated mixture in which the feed initially contacts a portion of the mixture which comprises essentially all one of the zeolites. The concentration of the second zeolite can be gradually increased, and the concentration of the first zeolite gradually decreased, in successive portions of the mixture until the mixture becomes essentially all second zeolite. Depending on the feed, reaction conditions, and desired product, the combination may be such that the feed initially contacts the MTT zeolite first or the GON zeolite first.

The combination of MTT and GON zeolites may also be used in layers. The use of catalyst layers is disclosed in U. S. Patent No. 5,149,421, issued September 22, 1992 to Miller, which is incorporated by reference herein its entirety. The order of the layers may be MTT in a first layer and GON in a subsequent layer, or vice versa.

Depending upon the nature of the feed and the desired products, the MTT and GON zeolites can be employed over a wide range of concentrations. The catalyst combination may comprise 1-99 weight percent MTT zeolite and 99-1 weight percent GON zeolite. Preferably, the crystal size of the zeolites is less than 0.1 micron, i.e., the longest dimension of the crystal is less than 0.1 micron.

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

The zeolite can be used in intimate combination with hydrogenating components, such as tungsten, vanadium, molybdenum, rhenium, nickel, cobalt, chromium, manganese or a noble metal, such as palladium or platinum.

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

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

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

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

The zeolites can be formed into a wide variety of physical shapes. Generally speaking, the zeolite can be in the form of a powder, a granule or a molded product, such as extrudate having a 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 with an organic binder, the zeolite can be extruded before drying, or dried or partially dried and then extruded.

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

The MTT and GON zeolites are used in dewaxing hydrocarbonaceous feedstocks. Hydrocarbonaceous feedstocks contain carbon compounds and can be from many different sources, such as virgin petroleum fractions, recycle petroleum fractions, shale oil, liquefied coal, tar sand oil, synthetic paraffins from NAO, recycled plastic feedstocks, bright stock, Fischer-Tropsch waxes (i.e., synthetic waxes derived from a Fischer Tropsch process, preferably an oxygenate-containing Fischer Tropsch process, boiling below about 700°F (371°C)) and, in general, can be any carbon containing feedstock susceptible to zeolitic catalytic dewaxing reactions. Depending on the type of processing the hydrocarbonaceous feed is to undergo, the feed can contain metal or be free of metals. It can also have high or low nitrogen or sulfur impurities. It can be appreciated, however, that in general processing will be more efficient (and the catalyst more active) the lower the metal, nitrogen, and sulfur content of the feedstock. Preferably, after treating the feedstock in

accordance with the present invention, the cloud point of the feedstock (depending on its original composition) is reduced to not more than 10°C.

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

Typical dewaxing reaction conditions which may be employed when using catalysts comprising a combination of zeolites MTT and GON in the dewaxing reactions of this invention include a temperature of about 200-475°C, preferably about 250-450°C, a pressure of about 15-3000 psig, preferably about 200-3000 psig, and a LHSV of about 0.1-20, preferably 0.2-10.

The MTT and GON combination, preferably predominantly in the hydrogen form, can be used to dewax hydrocarbonaceous feeds by selectively removing straight chain paraffins. Typically, the viscosity index of the dewaxed product is improved (compared to the waxy feed) when the waxy feed is contacted with a combination of zeolites MTT and GON under isomerization dewaxing conditions.

The catalytic dewaxing conditions are dependent in large measure on the feed used and upon the desired pour point. Hydrogen is preferably present in the reaction zone during the catalytic dewaxing process. The hydrogen to feed ratio is typically between about 500 and about 30,000 SCF/bbl (standard cubic feet per barrel), preferably about 1000 to about 20,000 SCF/bbl. Generally, hydrogen will be separated from the product and recycled to the reaction zone. Typical feedstocks include light gas oil, heavy gas oils and reduced crudes boiling above about 350°F (177°C).

A typical dewaxing process is the catalytic dewaxing of a hydrocarbon oil feedstock boiling above about 350°F (177°C) and containing straight chain and slightly branched chain hydrocarbons by contacting the hydrocarbon oil feedstock in the presence of added hydrogen gas at a hydrogen pressure of about 15-3000 psi with a catalyst comprising a combination of zeolites MTT and GON and at least one Group VIII metal.

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

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

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

The combination of MTT and GON may also be used to dewax raffinates, including bright stock, under conditions such as those disclosed in U. S. Patent No. 4,181,598, issued January 1, 1980 to Gillespie et al., which is incorporated by reference herein in its entirety.

It is often desirable to use mild hydrogenation (sometimes referred to as hydrofinishing) to produce more stable dewaxed products. The hydrofinishing step can be performed either before or after the dewaxing step, and preferably after. Hydrofinishing is typically conducted at temperatures ranging from about 190°C to about 340°C at pressures from about 400 psig to

about 3000 psig at space velocities (LHSV) between about 0.1 and 20 and a hydrogen recycle rate of about 400 to 1500 SCF/bbl. The hydrogenation catalyst employed must be active enough not only to hydrogenate the olefins, diolefins and color bodies which may be present, but also to reduce the aromatic content. Suitable hydrogenation catalyst are disclosed in U. S. Patent No. 4,921,594, issued May 1, 1990 to Miller, which is incorporated by reference herein in its entirety. The hydrofinishing step is beneficial in preparing an acceptably stable product (e.g., a lubricating oil) since dewaxed products prepared from hydrocracked stocks tend to be unstable to air and light and tend to form sludges spontaneously and quickly.

Lube oil may be prepared using a combination of zeolites MTT and GON. For example, a C_{20+} lube oil may be made by isomerizing a C_{20+} olefin feed over a catalyst comprising a combination of zeolites MTT and GON, preferably predominantly in the hydrogen form, and at least one Group VIII metal. Alternatively, the lubricating oil may be made by hydrocracking in a hydrocracking zone a hydrocarbonaceous feedstock to obtain an effluent comprising a hydrocracked oil, and catalytically dewaxing the effluent at a temperature of at least about 400°F (204°C) and at a pressure of from about 15 psig to about 3000 psig in the presence of added hydrogen gas with a catalyst comprising a combination of zeolites MTT and GON, preferably predominantly in the hydrogen form, and at least one Group VIII metal.

WHAT IS CLAIMED IS:

1. A dewaxing process comprising contacting a hydrocarbon feedstock under dewaxing conditions with a catalyst comprising a combination of zeolites having the MTT and GON framework topologies defined by the connectivity of their tetrahedral atoms.

2. The process of Claim 1 wherein the zeolites are predominantly in the hydrogen form.

3. The process of Claim 1 wherein the catalyst further comprises at least one Group VIII metal.

4. The process of Claim 1 wherein the feedstock is bright stock.

5. The process of Claim 1 wherein the feedstock is derived from a Fischer Tropsch process.

6. The process of Claim 1 wherein the MTT and GON zeolites have a crystal size less than 0.1 micron.

7. A process for improving the viscosity index of a dewaxed product of waxy hydrocarbon feeds comprising contacting a waxy hydrocarbon feed under isomerization dewaxing conditions with a catalyst comprising a combination of zeolites having the MTT and GON framework topologies defined by the connectivity of their tetrahedral atoms.

8. The process of Claim 7 wherein the zeolites are predominantly in the hydrogen form.

9. The process of Claim 7 wherein the catalyst further comprises at least one Group VIII metal.

10. A process for producing a C_{20+} lube oil from a C_{20+} olefin feed comprising isomerizing said olefin feed under isomerization conditions over a catalyst comprising a combination of zeolites having the MTT and GON framework topologies defined by the connectivity of their tetrahedral atoms.

11. The process of Claim 10 wherein the zeolites are predominantly in the hydrogen form.

12. The process of Claim 10 wherein the catalyst further comprises at least one Group VIII metal.

13. A process for catalytically dewaxing a hydrocarbon oil feedstock boiling above about 350°F (177°C) and containing straight chain and slightly branched chain hydrocarbons comprising contacting said hydrocarbon oil feedstock in the presence of added hydrogen gas at a hydrogen pressure of about 15-3000 psi under dewaxing conditions with a catalyst comprising a combination of zeolites having the MTT and GON framework topologies defined by the connectivity of their tetrahedral atoms.

14. The process of Claim 13 wherein the zeolites are predominantly in the hydrogen form.

15. The process of Claim 13 wherein the catalyst further comprises at least one Group VIII metal.

16. A process for isomerization dewaxing a raffinate comprising contacting said raffinate in the presence of added hydrogen under isomerization dewaxing conditions with a catalyst comprising a combination of zeolites having the MTT and GON framework topologies defined by the connectivity of their tetrahedral atoms.

17. The process of Claim 16 wherein the zeolites are predominantly in the hydrogen form.

18. The process of Claim 16 wherein the catalyst further comprises at least one Group VIII metal.

19. The process of Claim 16 wherein the raffinate is bright stock.

20. A process for reducing the cloud point of a hydrocarbon feed comprising contacting a hydrocarbon oil feedstock which has a major portion boiling over 1000°F (538°C) with a catalyst system comprising a combination of a zeolite having MTT topology and a zeolite having GON topology, wherein at least a portion of said feedstock is converted.

21. The process of Claim 20 wherein the catalyst system further comprises a hydrogenation component.

22. The process of Claim 20 wherein the cloud point of the feedstock is reduced to not more than 10°C.

23. The process of Claim 21 wherein the hydrogenation component comprises a Group VIII metal.

24. The process of claim 23 wherein the Group VIII metal is selected from platinum, palladium and mixtures thereof.

25. The process of Claim 20 wherein the process is a dewaxing process and wherein the contacting is conducted under dewaxing conditions.

26. The process of Claim 20 wherein the hydrocarbon oil is bright stock.

27. The process of Claim 20 wherein the hydrocarbon oil is derived from a Fischer-Tropsch wax.

28. The process of Claim 20 wherein the process is conducted in the presence of added hydrogen gas.

29. The process of Claim 20 wherein the MTT and GON zeolites are aluminosilicates.

30. The process of Claim 20 wherein the MTT and GON zeolites have a crystal size less than about 0.1 micron.