

SELECTIVE DEHYDRATION OF ALCOHOLS TO DIALKYLETHERS
AND INTEGRATED ALCOHOL-TO-GASOLINE PROCESSES

FIELD OF THE INVENTION

[0001] This disclosure relates to the selective dehydration of alcohols to dialkyl ethers, as well as integrated processes for alcohol-to-gasoline formation including such selective dehydration as a first step.

BACKGROUND OF THE INVENTION

[0002] The selective dehydration of methanol to produce dimethyl ether is a commercially important reaction as the first step in the conversion of methanol to gasoline and diesel boiling range hydrocarbons. Similarly, the selective dehydration of higher alcohols, such as ethanol, is important in the synthesis of a number of commercially significant dialkyl ethers, such as diethyl ether.

[0003] As discussed in, for example, U.S. Patent No. 4,536,485, current processes for the selective dehydration of alcohols employ a solid acid catalyst, such as alumina, silica, alumina-silica mixtures and crystalline aluminosilicates, *e.g.*, zeolites. However, these solid acid catalysts frequently produce undesirable by-products, such as coke, methane, carbon dioxide, and hydrogen, in addition to the desired ether product. By-product formation typically reduces selectivity and can trigger potentially dangerous temperature excursions within an adiabatic reactor. Therefore, by-product formation can be kept low by adjusting the water concentration of the alcohol feed to control reactor outlet temperature. However, increasing the water concentration of the alcohol feed can reduce the equilibrium conversion of the alcohol per reactor pass and can lower overall selective dehydration process efficiency.

[0004] According to the present invention, it has now been found that C₁-C₄ alcohols, such as methanol, can be selectively dehydrated to dialkylethers without significant byproduct formation or reactor temperature excursions even at relatively low water concentrations in the alcohol feed by selecting as the selective dehydration catalyst a form of γ -alumina that is substantially free of terminal hydroxyl groups on tetrahedrally coordinated aluminum sites, as determined by the substantial absence of an absorbance band at $\sim 3770\text{ cm}^{-1}$ in the IR spectrum of the catalyst.

SUMMARY OF THE INVENTION

[0005] In one aspect, the invention resides in an integrated process for converting a C₁-C₄ alcohol to gasoline and/or diesel boiling range product, said process comprising: contacting a C₁-C₄ alcohol feed under selectively dehydrating conditions with a catalyst comprising γ -alumina which is substantially free of terminal hydroxyl groups on tetrahedrally coordinated aluminum sites of the catalyst to form a dialkylether dehydration product; and contacting the dialkylether dehydration product with a zeolite conversion catalyst under conversion conditions to form the gasoline and/or diesel boiling range hydrocarbon product.

[0006] Conveniently, the γ -alumina of the selective dehydration catalyst can exhibit an IR spectrum having a normalized absorbance at $\sim 3770\text{ cm}^{-1}$ of less than 0.010 cm/mg.

[0007] Additionally or alternately, the selective dehydration catalyst can have an alpha value of less than 1.

[0008] Additionally or alternately, the selective dehydration catalyst, when used to isomerize 2-methyl-2-pentene at $\sim 350^\circ\text{C}$, approximately atmospheric pressure, and a weight hourly space velocity of $\sim 2.4\text{ hr}^{-1}$, can produce an isomerized product in which the weight ratio of 2,3 dimethyl-2 butene to 4-methyl-2-pentene is less than 0.2.

[0009] Additionally or alternately, the dehydration conditions can include a temperature from about 250°C to about 500°C and a pressure from about 100 kPa to about 7000 kPa.

[0010] Additionally or alternately, the C₁-C₄ alcohol feed can comprise less than 15 wt% water.

[0011] In a particular embodiment, the alcohol can comprise or be methanol, and the dialkyl ether can thus comprise or be dimethyl ether, in which case the conversion step advantageously forms both gasoline and diesel boiling range hydrocarbons in its product.

[0001] It should be noted that this application is related to U.S. Provisional Application Nos. 61/548,015, 61/548,038, 61/548,044, 61/548,052, 61/548,057, and 61/548,064, each filed on October 17, 2011, the entire contents of each of which are hereby incorporated by reference herein, to the extent necessary to describe any portion of the instant invention detailed therein. This application is also related to five other co-pending international (PCT) applications, each filed on even date herewith and claiming the benefit to the aforementioned U.S. provisional patent applications, and which are

entitled “Process for Producing Phosphorus Modified Zeolite Catalysts”, “Process for Producing Phosphorus Modified Zeolite Catalysts”, “Phosphorus Modified Zeolite Catalysts”, “Phosphorus Modified Zeolite Catalysts”, and “Phosphorus Modified Zeolite Catalysts”, respectively, the entire contents of each of which are hereby further incorporated by reference herein, to the extent necessary to describe any portion of the instant invention detailed therein.

BRIEF DESCRIPTION OF THE DRAWINGS

[0002] Figure 1 shows a graph plotting methanol conversion and dimethyl ether and methane production against temperature in the methanol dehydration process of Example 1.

[0003] Figure 2 shows a graph plotting the weight fraction of methane produced against temperature in the methanol dehydration process of Example 1, with and without the addition of ~10 wt% water to the methanol feed.

[0004] Figure 3 shows a graph plotting the weight fraction of methane produced against temperature for the different γ -alumina catalysts employed in the methanol dehydration process of Example 2.

[0005] Figure 4 shows a graph comparing the product slates obtained with the different γ -alumina catalysts employed in the 2-methyl-2-pentene isomerization process of Example 3.

[0006] Figure 5 shows a graph comparing the concentration of Lewis acids sites for the different γ -alumina catalysts employed in the methanol dehydration process of Example 2.

[0007] Figure 6 compares the difference IR spectra for the γ -alumina catalysts employed in the methanol dehydration process of Example 2 after pyridine adsorption at ~150°C, followed by evacuation for ~30 minutes at ~150°C, and after outgassing for ~2 hours at ~450°C under vacuum.

[0008] Figure 7 shows a plot of methane formation at ~440°C against concentration of hydroxyl groups at ~3771 cm^{-1} for the different γ -alumina catalysts employed in the methanol dehydration process of Example 2.

DETAILED DESCRIPTION OF THE EMBODIMENTS

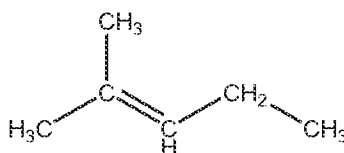
[0009] Described herein is an integrated process for converting a C₁-C₄ alcohol to gasoline and/or diesel boiling range product. As a first step, the integrated process comprises selective dehydration of an alcohol to a dialkylether using a catalyst comprising γ -alumina that is substantially free of terminal hydroxyl groups on tetrahedrally coordinated aluminum sites of the selective dehydration catalyst. The second step can advantageously include contacting the dialkylether dehydration product with a zeolite conversion catalyst under conversion conditions to form the gasoline and/or diesel boiling range hydrocarbon product.

[0010] The alcohol dehydration can generally take place at a temperature ranging from about 250°C to about 500°C and at a pressure from about 100 kPa to about 7000 kPa. At higher operating temperatures, it has been found that the presence of strong Lewis acidity on the selective dehydration catalyst can lead to non-selective alcohol decomposition to coke, methane, carbon dioxide, and hydrogen by-products, tending to result in loss of yields, deactivation, and potentially dangerous temperature rise in commercial reactors. By selecting an alumina without strong Lewis acidity and substantially free of terminal [OH-] groups on the tetra-coordinated alumina sites (indicated by an absorbance band at $\sim 3770\text{ cm}^{-1}$ in the pyridine IR spectra), alcohol decomposition can be significantly reduced without significantly negatively impacting the alcohol dehydration reaction. In particular, it has been found that advantageous results were obtained when the γ -alumina of the selective dehydration catalyst has a normalized IR absorbance at $\sim 3770\text{ cm}^{-1}$ of less than 10 cm/g.

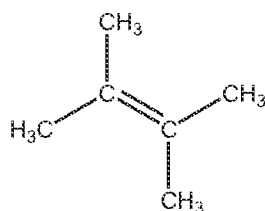
[0011] As used herein, the term “normalized absorbance at $\sim 3770\text{ cm}^{-1}$ ” is used herein to mean a difference between the absorbance centered at about 3770 cm^{-1} in the pyridine FTIR spectrum of the selective dehydration catalyst comprising γ -alumina and the corresponding absorbance centered at about 3770 cm^{-1} in the background spectrum of the selective dehydration catalyst comprising γ -alumina, divided by the weight of the sample per unit area. In this test, the background FTIR spectrum is taken at a temperature T between $\sim 20^\circ\text{C}$ and $\sim 80^\circ\text{C}$ after outgassing the sample at about $\sim 450^\circ\text{C}$ under vacuum, including a pressure P of about 1.3 mPa or less for at least ~ 1 hour. The pyridine FTIR spectrum is taken at the same temperature T after (i) outgassing the sample at about 450°C under vacuum, including a pressure P of about 1.3 mPa or less for at least ~ 1 hour, (ii)

cooling the sample to about 150°C, (iii) allowing the sample to adsorb pyridine under a pyridine partial pressure of about 18 torr (about 2.4 kPa) at about 150°C for at least ~20 minutes, (iv) evacuating the sample at about 150°C and said pressure P for at least ~20 minutes, and (v) then cooling the sample to said temperature T.

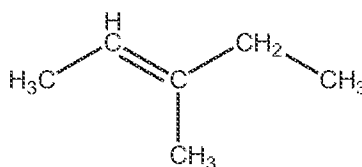
[0012] The absence of strong Lewis acidity in the preferred catalysts employed herein can be conveniently demonstrated by investigating the product slate when the catalyst is used to isomerize 2-methyl-2-pentene:



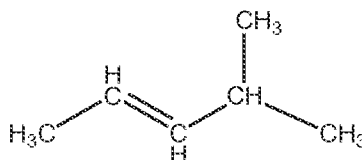
[0013] Thus, as discussed by G.M. Kramer and G.B. McVicker, *Acc. Chem. Res.* **19** (1986), p. 78, the presence of strong acid sites on the catalyst can tend to favor the production of 2,3 dimethyl-2 butene:



whereas sites of intermediate strength can tend to favor 3-methyl-2-pentene:



and weak acid sites can tend to favor 4-methyl-2-pentene:



[0014] In particular, it has been found that advantageous results can be obtained in the present selective dehydration process using an γ -alumina, which, when employed to isomerize 2-methyl-2-pentene at ~350°C, atmospheric pressure, and a weight hourly space velocity of ~2.4 hr⁻¹, can produce an isomerized product in which the weight ratio of 2,3-dimethyl-2-butene to 4-methyl-2-pentene can be less than 0.2, *e.g.*, less than 0.05.

[0015] Preferably, the selective dehydration catalyst employed in the present process can have an alpha value less than 1. Alpha value can be a measure of the acid activity of a zeolite catalyst, as compared with a standard silica-alumina catalyst. The alpha test is described in U.S. Patent No. 3,354,078; in the Journal of Catalysis, v. 4, p. 527 (1965); v. 6, p. 278 (1966); and v. 61, p. 395 (1980), each incorporated herein by reference as to that description. The experimental conditions of the test used herein included a constant temperature of ~538°C and a variable flow rate, as described in detail in the Journal of Catalysis, v. 61, p. 395.

[0016] The selective alcohol dehydration process described herein may be conducted in the presence of water, but generally the water concentration of the alcohol feed can be lower than that required with conventional catalysts, thereby advantageously increasing the equilibrium conversion of the alcohol per reactor pass and/or raising overall process efficiency. Typically, the C₁-C₄ alcohol feed can comprise less than 15 wt% water, for example less than 10 wt% water, less than 7 wt% water, or less than 4 wt%, water. Additionally or alternately, the C₁-C₄ alcohol feed can comprise at least 0.5 wt% water, for example at least 2 wt% water.

[0017] The present process can be used to selectively dehydrate a wide variety of alcohols to their corresponding dialkylethers, although generally the process can be employed with n-alcohols having from 1 to 6 carbons atoms, preferably 1 to 4 carbons, especially methanol and/or ethanol. By using the selective dehydration catalyst described herein, it can be possible to reduce the amount of alkane by-product to less than 1 wt% of the selective dehydration conversion products. In a particular embodiment, the alcohol can comprise or be methanol, and the dialkylether can comprise or be dimethylether. Generally, the integrated process can further comprise a conversion step of contacting at least part of the dialkylether (*e.g.*, dimethylether) selective dehydration product with a zeolite conversion catalyst under conversion conditions to form a gasoline and/or diesel boiling range hydrocarbon product.

[0018] The invention can additionally or alternately include one or more of the following embodiments.

[0019] Embodiment 1. An integrated process for converting a C₁-C₄ alcohol to gasoline and/or diesel boiling range product, said process comprising: contacting a C₁-C₄ alcohol feed under selectively dehydrating conditions with a catalyst comprising γ -

alumina which is substantially free of terminal hydroxyl groups on tetrahedrally coordinated aluminum sites of the catalyst to form a dialkylether dehydration product; and contacting the dialkylether dehydration product with a zeolite conversion catalyst under conversion conditions to form the gasoline and/or diesel boiling range hydrocarbon product.

[0020] Embodiment 2. The process of embodiment 1, wherein the γ -alumina of the selective dehydration catalyst has a normalized IR absorbance at $\sim 3770\text{ cm}^{-1}$ of less than 10 cm/g.

[0021] Embodiment 3. The process of any one of the previous embodiments, wherein the selective dehydration catalyst has an alpha value less than 1.

[0022] Embodiment 4. The process of any one of the previous embodiments, wherein the selective dehydration catalyst, when used to isomerize 2-methyl-2-pentene at $\sim 350^\circ\text{C}$, approximately atmospheric pressure, and a weight hourly space velocity of about 2.4, produces an isomerized product in which the weight ratio of 2,3 dimethyl-2 butene to 4-methyl-2-pentene is less than 0.2.

[0023] Embodiment 5. The process of any one of the previous embodiments, wherein the selectively dehydrating conditions include a temperature from about 250°C to about 500°C and a pressure from about 100 kPa to about 700 kPa.

[0024] Embodiment 6. The process of any one of the previous embodiments, wherein the C_1 - C_4 alcohol feed comprises less than 15 wt% water.

[0025] Embodiment 7. The process of any one of the previous embodiments, wherein the dialkylether product contains less than 1 wt% of the corresponding alkane.

[0026] Embodiment 8. The process of any one of the previous embodiments, wherein the C_1 - C_4 alcohol comprises or is methanol, and wherein the dialkylether comprises or is dimethylether.

[0027] Embodiment 9. The process of embodiment 8, wherein the conversion step results in a product comprising both gasoline and diesel boiling range hydrocarbons.

[0028] The invention will now be more particularly described with reference to the following non-limiting Examples and the accompanying drawings.

EXAMPLES**Example 1**

[0029] ~50-gram samples of a commercially available γ -alumina designated herein as catalyst 1 were tested in the dehydration of ~100% methanol at ~55 psig (~380 kPag), ~10 hr⁻¹ WHSV, and a variety of temperatures of ~380°C, ~400°C, ~420°C, and ~440°C. The results are shown in Figure 1. In each case, the methanol was dehydrated to an equilibrium mixture of dimethylether and methanol. However, a significant amount of methane was formed from methanol decomposition, particularly at higher temperatures.

[0030] The process was repeated with the addition of ~10 wt% water to the methanol feed, and the results are shown in Figure 2, which also plots the results for a silicon carbide control (no methanol dehydration or decomposition). It can be seen that increasing the water content of the methanol feed to ~10 wt% significantly reduced non-selective methanol decomposition and methane formation. However, methane formation was still higher than desired.

Example 2

[0031] The process of Example 1 was repeated, but using the three different commercially available γ -aluminas summarized in Table 1 below to effect dehydration of ~100% methanol. The results are shown in Figure 3 and demonstrate that the best results appeared to be obtained with Catalyst 3.

Table 1

Alumina Catalyst	2	1	3	4
Shape	Extrudate	Extrudate	1/8" sphere	1/16" Cylinder
Surface area, m ² /g	~216	~193	~191	~88
Particle density, g/cc	~1.15	~1.28	~1.13	~1.33
Pore volume, cc/g	~0.61	~0.44	~0.47	~0.43
Alpha activity	~3.7	~2.7	~0.91	~2.2
TPAA*, meq/g	~0.43	~0.44	~0.26	~0.15
Trace metals by XRF, wt%				
Na	~0.07	~0.07	~0.095	nd
Si	~0.02	~0.023	~0.033	~0.036
S	nd	~0.003	~0.0061	~0.0048
Cl	nd	nd	nd	nd
Fe	~0.0026	~0.015	~0.01	~0.0043

*TPAA = temperature programmed ammonia adsorption

[0032] Samples of the γ -alumina were screened for acidic activity with n-hexane cracking measurements in a routine alpha test at standard conditions (~ 100 torr hexane vapor pressure in a He carrier gas flowing through a reactor held at $\sim 1000^\circ\text{F}$). The alpha test consisted of four evenly-spaced measurements over ~ 30 minutes. The data was plotted, and the relative rate of cracking was calculated relative to silica-alumina, which is defined to have an alpha value of 1. The results are shown in Table 1 above.

Example 3

[0033] The gas phase isomerization of 2-methyl-2-pentene (2M2P) over each of the catalysts employed in Example 2 was studied in a plug-flow reactor. An amount of ~ 0.1 g of each catalyst was pretreated in flowing helium for about 1 hour at ~ 723 K prior to the reaction. The reaction was initially conducted at ~ 473 K for ~ 1 hour, while a flow of ~ 15 mL/min of ~ 7 vol% 2M2P in helium at approximately atmospheric pressure was passed over the catalyst. The feed was then switched to helium and the catalyst cooled to ~ 448 K and then to ~ 423 K. The catalyst samples were taken ~ 10 minutes after switching on the feed at ~ 473 K, ~ 448 K, and ~ 423 K. The products were analyzed by GC with an FID detector, and the results are summarized in Figure 4.

[0034] It can be seen that the Catalyst 1 appeared to be the most acidic alumina, with about 50% of medium and strong acid sites, whereas the alumina of Catalyst 3 appeared to have almost no strong acid sites, and less acid sites overall than the other aluminas.

Example 4

[0035] For IR measurements of adsorbed pyridine, samples of the catalysts employed in Example 2 were ground and pressed into thin self-supporting wafers. Specific wafer weights ranged from about $20\text{--}35$ mg/cm². Each wafer was placed in an IR transmission cell equipped with CaF₂ windows. The IR cuvette could be heated and evacuated. For the sample treatment, the cuvette was connected to a high-vacuum manifold. A pressure of $\sim 2 \times 10^{-6}$ torr (~ 0.3 mPa) measured by an ion gauge could be achieved in the manifold using a turbo molecular pump. The adsorption of pyridine was carried out from a glass vial attached to the manifold. The pyridine partial pressure was measured by a BaratronTM. For the IR measurement, the sample cuvette was transferred into a NicoletTM

670 FTIR spectrometer. Spectra were taken at $\sim 2\text{ cm}^{-1}$ resolution accumulating approximately 512 scans.

[0036] Before loading each wafer, the IR cuvette was outgassed in flowing air at a flow rate of about 50 ml/min for ~ 2 hours at $\sim 520^\circ\text{C}$ in order to remove trace amounts of pyridine that might be adsorbed on the walls of the cuvette from the previous experiment. The catalyst wafer was then placed into the regenerated cuvette and evacuated for ~ 2 hours at $\sim 450^\circ\text{C}$ in order to remove physisorbed water and to activate the sample. The sample cooled under vacuum to $\sim 80^\circ\text{C}$ under a final pressure of about 2×10^{-6} torr (~ 0.3 mPa). In this state, the cuvette was disconnected from the manifold and a spectrum was taken from the outgassed sample. This spectrum was referred to as background spectrum.

[0037] For the adsorption of pyridine, the cuvette was reconnected to the manifold, and pyridine was allowed to equilibrate with its vapor for ~ 20 minutes at room temperature ($\sim 23^\circ\text{C}$) leading to pyridine partial pressures of about 18 torr (~ 2.4 kPa). During this time the valve to the cuvette was shut, and the sample was heated to $\sim 150^\circ\text{C}$. After the temperature of the cuvette reached $\sim 150^\circ\text{C}$, the valve to the liquid pyridine vial was closed, and pyridine vapor was expanded into the cell. The sample was exposed to pyridine vapor at $\sim 150^\circ\text{C}$ for ~ 30 minutes, then evacuated for another ~ 30 minutes at $\sim 150^\circ\text{C}$, and subsequently cooled to $\sim 80^\circ\text{C}$ under vacuum. The final pressure was between $\sim 5 \times 10^{-6}$ and $\sim 1 \times 10^{-5}$ torr. A sample spectrum was taken of the catalyst with adsorbed pyridine. The amount of pyridine adsorbed on the sample after adsorption and evacuation of pyridine at $\sim 150^\circ\text{C}$ was referred to as the total amount of weakly and strongly bonded pyridine corresponding to the amount of weak and strong Lewis acid sites, respectively.

[0038] After the adsorption of pyridine at $\sim 150^\circ\text{C}$ and subsequent evacuation of the cell at $\sim 150^\circ\text{C}$, the cell was again reconnected to the manifold and continued to be evacuated for ~ 30 minutes at $\sim 450^\circ\text{C}$. After cooling down to $\sim 80^\circ\text{C}$, another sample spectrum was collected. The amount of pyridine left on the sample after evacuation at $\sim 450^\circ\text{C}$ was referred to as strongly bonded pyridine corresponding to the amount of strong Lewis acid sites.

[0039] The band for the 19b ring vibration of Lewis-bonded pyridine with peak position between $\sim 1450\text{ cm}^{-1}$ and $\sim 1455\text{ cm}^{-1}$ was chosen for the evaluation of Lewis acid sites. The baseline for this band was defined as a linear curve between the minima to the

high frequency and low frequency side of the band. The Lewis band was integrated between limits at $\sim 1470\text{ cm}^{-1}$ and $\sim 1420\text{ cm}^{-1}$, and the integration limits were set to coincide with the points defining the baseline. The band for the 19a ring vibration of pyridinium ions with peak position between $\sim 1540\text{ cm}^{-1}$ and $\sim 1545\text{ cm}^{-1}$, which corresponded to Bronsted acid sites, was not observed in the present study. The amount of Lewis-bonded pyridine per gram of sample was calculated using Beer-Lambert's law given in equations 1) and 2):

$$\begin{aligned} 1) \quad A_i / \epsilon_i &= c * d \\ 2) \quad A_i / \epsilon_i &= n / Q \end{aligned}$$

where

A_i : integrated absorbance [cm^{-1}]

ϵ_i : integrated molar extinction coefficient [$\text{cm}/\mu\text{mol}$]

c : concentration of pyridine adsorbed in the wafer [$\mu\text{mol}/\text{cm}^3$]

d : wafer thickness [cm]

Q : geometric surface area of wafer [cm^2]

n : amount of pyridine [μmol]

[0040] The integrated molar extinction coefficient was adopted from the literature to be $\epsilon_L \approx 2.22\text{ cm}/\mu\text{mol}$ for Lewis-bonded pyridine. Reformulation of equation 1) and dividing by the wafer mass, m [mg], yielded equation 3):

$$3) \quad n / m = (A_i * Q) / (\epsilon_i * m)$$

which expressed the amount of pyridine in mmol adsorbed per gram of sample.

[0041] The concentration of a particular Lewis acid-Bronsted base pair site containing a hydroxyl group with an OH stretching frequency between $\sim 3770\text{ cm}^{-1}$ and $\sim 3772\text{ cm}^{-1}$ was determined from the change in absorbance at $\sim 3771\text{ cm}^{-1}$ upon adsorption of pyridine. Normalization by the specific wafer weight yielded equation 4:

$$4) \quad c[\text{OH } \sim 3771\text{ cm}^{-1}] = (A[\sim 3771\text{ cm}^{-1}, \text{py } \sim 150^\circ\text{C}] - A[\sim 3771\text{ cm}^{-1}, \text{vac } \sim 450^\circ\text{C}]) / (m/Q)$$

[0042] The difference spectrum [py $\sim 150^\circ\text{C}$]–[vac $\sim 450^\circ\text{C}$] produced a minimum at the position of the OH band at $\sim 3771\text{ cm}^{-1}$, relative to the high frequency region neighboring the OH stretching regime. The intensity of the $\sim 3771\text{ cm}^{-1}$ band was defined as the difference in absorbance between the minimum at $\sim 3771\text{ cm}^{-1}$ and the baseline at $\sim 3850\text{ cm}^{-1}$. The corresponding concentration of the hydroxyl groups at $\sim 3771\text{ cm}^{-1}$, as defined in equation 4, has units of [$\text{cm}/\text{mg sample}$].

[0043] Figure 5 shows the amount of the total number of Lewis acid sites after pyridine adsorption and evacuation at $\sim 150^\circ\text{C}$, and that of strongly bonded pyridine

evaluated after subsequent evacuation at $\sim 450^{\circ}\text{C}$. It can be seen that the total number of Lewis sites increased in the order of Catalyst 4 < Catalyst 3 < Catalyst 2 $\approx$ Catalyst 1, while the amount of strong Lewis acid sites followed the order of Catalyst 4 $\approx$ Catalyst 3 < Catalyst 2 $\approx$ Catalyst 1. No Bronsted acid sites were detected by IR of adsorbed pyridine.

[0044] Figure 6 shows the difference spectra in the range of OH stretching frequencies of the alumina samples formed by subtracting the background spectra after outgassing for ~ 2 hours in vacuum at $\sim 450^{\circ}\text{C}$ from the sample spectra taken after adsorption of pyridine and subsequent evacuation at $\sim 150^{\circ}\text{C}$.

[0045] Pyridine was observed to interact by H-bonding with the hydroxyl group at $\sim 3771\text{ cm}^{-1}$, producing a new OH band for the perturbed hydroxyl group which was shifted to lower frequencies. The H-bonding led to the disappearance of the band at $\sim 3771\text{ cm}^{-1}$. Consequently, H-bonding produced a negative band at the position of the unperturbed OH stretching frequency at $\sim 3771\text{ cm}^{-1}$ in the difference spectrum between the sample spectrum taken after pyridine adsorption at $\sim 150^{\circ}\text{C}$ and the background spectrum taken after outgassing at $\sim 450^{\circ}\text{C}$.

[0046] Figure 7 shows a correlation between the concentration of the hydroxyl group at $\sim 3771\text{ cm}^{-1}$ and the wt% methane made over the alumina in the DME reactor at $\sim 440^{\circ}\text{C}$. The activity of the catalyst to convert methanol into methane increased approximately linearly with the concentration of the hydroxyl group at $\sim 3771\text{ cm}^{-1}$.

[0047] While the present invention has been described and illustrated by reference to particular embodiments, those of ordinary skill in the art will appreciate that the invention lends itself to variations not necessarily illustrated herein. For this reason, then, reference should be made solely to the appended claims for purposes of determining the true scope of the present invention.

CLAIMS

What is claimed is:

1. An integrated process for converting a C₁-C₄ alcohol to gasoline and/or diesel boiling range product, said process comprising:
 - contacting a C₁-C₄ alcohol feed under selectively dehydrating conditions with a catalyst comprising γ -alumina which is substantially free of terminal hydroxyl groups on tetrahedrally coordinated aluminum sites of the catalyst to form a dialkylether dehydration product; and
 - contacting the dialkylether dehydration product with a zeolite conversion catalyst under conversion conditions to form the gasoline and/or diesel boiling range hydrocarbon product.
2. The process of claim 1, wherein the γ -alumina of the selective dehydration catalyst has a normalized IR absorbance at $\sim 3770\text{ cm}^{-1}$ of less than 10 cm/g.
3. The process of claim 1 or claim 2, wherein the selective dehydration catalyst has an alpha value less than 1.
4. The process of any one of the previous claims, wherein the selective dehydration catalyst, when used to isomerize 2-methyl-2-pentene at $\sim 350^\circ\text{C}$, approximately atmospheric pressure, and a weight hourly space velocity of about 2.4, produces an isomerized product in which the weight ratio of 2,3 dimethyl-2 butene to 4-methyl-2-pentene is less than 0.2.
5. The process of any one of the previous claims, wherein the selectively dehydrating conditions include a temperature from about 250°C to about 500°C and a pressure from about 100 kPa to about 700 kPa.
6. The process of any one of the previous claims, wherein the C₁-C₄ alcohol feed comprises less than 15 wt% water.
7. The process of any one of the previous claims, wherein the dialkylether product

contains less than 1 wt% of the corresponding alkane.\

8. The process of any one of the previous claims, wherein the C₁-C₄ alcohol is methanol, and wherein the dialkylether is dimethylether.
9. The process of claim 8, wherein the conversion step results in a product comprising both gasoline and diesel boiling range hydrocarbons.