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(54) Titre : CATALYSEURS DESALUMINES POUR L'ALKYLATION AROMATIQUE
(54) Title: DEALUMINATED CATALYSTS FOR AROMATIC ALKYLATION

(57) Abrégé/Abstract:
A catalyst composition is disclosed comprising a zeolite having a non-framework aluminum content of about less than 25 percent of the total aluminum content, a bulk silica:alumina ratio of about 6.5 to about 10.0 and a unit cell size ranging from about 2.440 to about 2.464 nm.

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(54) Title: PRODUCTION OF ALKYLATED AROMATIC COMPOUNDS USING DEALUMINATED CATALYSTS

(57) Abstract: A catalyst composition is disclosed comprising a zeolite having a non-framework aluminum content of about less than 25 percent of the total aluminum content, a bulk silica:alumina ratio of about 6.5 to about 10.0 and a unit cell size ranging from about 2.440 to about 2.464 nm.

DEALUMINATED CATALYSTS FOR AROMATIC ALKYLATION

Field of the Invention

This invention relates to the production of alkylated aromatic compounds such as, for example, alkyl naphthalenes and substituted alkyl naphthalenes.

Background of the Invention

Alkylaromatic fluids have been proposed for use as certain types of functional fluids in which good thermal and oxidative properties are required. For example, U.S. Patent No. 4,714,794 describes the monoalkylated naphthalenes as having excellent thermal and oxidative stability, low vapor pressure and flash point, good fluidity and high heat transfer capacity and other properties which render them suitable for use as thermal medium oils. The use of a mixture of monoalkylated and polyalkylated naphthalenes as a base for synthetic functional fluids is described in U.S. Pat. No. 4,604,491. U.S. Pat. Nos. 4,211,665 and 4,238,343 describe the use of alkylaromatics as transformer oils.

Alkylated naphthalenes are usually produced by the alkylation of naphthalene or a substituted naphthalene in the presence of an acidic alkylation catalyst such as a Friedel-Crafts catalyst, for example, an acidic clay as described in U.S. Pat. Nos. 4,714,794 or 4,604,491, or a Lewis acid such as aluminum trichloride as described in U.S. Pat. Nos. 4,211,665 and 4,238,343. The use of a collapsed silica-alumina zeolite for the catalytic alkylation of aromatic compounds such as naphthalene is disclosed in U.S. Pat. No. 4,570,027. The use of various zeolites including intermediate pore size zeolites such as ZSM-5 and large pore size zeolites such as zeolite L and ZSM-4 for the alkylation of various monocyclic aromatics such as benzene is disclosed in U.S. Pat. No. 4,301,316.

In the formulation of functional fluids based on the alkyl naphthalenes, it has been found that the preferred alkyl naphthalenes

include the mono-substituted naphthalenes since they provide the best combination of properties in the finished product. Because the mono-alkylated naphthalenes posses fewer benzylic hydrogens than the corresponding di-substituted or polysubstituted versions, they have better oxidative stability and therefore form better functional fluids and additives. In addition, the mono-substituted naphthalenes have a kinematic viscosity in the desirable range of about 5-8 cSt (at 100 °C) when having alkyl substituents of about 14 to about 18 carbon atoms chain length. Although the mono-alkylated naphthalenes may be obtained in admixture with more highly alkylated naphthalenes using conventional Friedel-Crafts catalysts such as those mentioned above, or by the use of zeolites such as USY, the selectivity to the desired mono-alkylated naphthalenes is not as high as desired.

Several recent advances have been made in this area which improve the yields of the desired mono-alkylated naphthenes.

U.S. Pat. No. 5,034,563 to Ashjian *et al.* teaches use of a zeolite containing a bulky cation. The use of, e.g., USY with cations having a radius of at least about 2.5 Angstroms increases selectivity for desired products. Taught as suitable were zeolites containing hydrated cations of metals of Group IA, divalent cations, especially of Group IIA, and cations of the Rare Earths. The patent had examples in which H^+, NH_4^+, and Na^+ were added to USY zeolite by a procedure involving forming a slurry of zeolite and liquid, 1 hour of stirring, decantation, and a repeat of the exchange procedure.

U.S. Pat. No. 5,177,284 discusses the desirable properties of alkylated naphthalene fluids with higher alpha:beta ratios, including improved thermal and oxidative stability. Le *et al.* found that several parameters influenced the alpha:beta ratio of the alkylated naphthalene products, including steaming the zeolite, lowering the alkylation temperature, or the use of acid-treated clay. Steamed USY catalyst gave excellent results in the examples. The

patent also discloses use of zeolites with reduced activity due to base exchange, alkaline earth ion exchange, and use of boron-zeolite beta.

U.S. Pat. No. 5,191,135 discloses the effect of co-feeding water for this reaction when using a large pore zeolite catalyst, such as zeolite Y. Adding from 1- 3 wt% water to the feed improved the alkylation reaction, a result attributed to suppression of zeolite acid site activity.

U.S. Pat. No. 5,191,134 disclosed a similar alkylation process using MCM-41.

U.S. Patent No. 5,457,254 to Ardito *et al.* discloses a naphthalene alkylation process whereby the presence of both ammonium and protonic species increases selectivity for production of long chain mono-alkyl substituted naphthalenes.

The present inventors did additional work to further improve this alkylation process, and to increase the efficiency of the reaction both in terms of conversion and yield.

The present inventors have discovered that an alkylation catalyst comprising a large pore zeolite which has been dealuminated to remove non-framework aluminum by selective ion exchange in acidic conditions, provides unexpectedly superior activity over a corresponding catalyst without the dealumination treatment. The inventors also discovered that the catalyst of the invention is effective in alkylation of other compounds containing two aromatic rings including, but not limited to, diphenyl oxide, diphenyl sulfide, diphenyl methane, and biphenyl.

Summary of the Invention

Accordingly, the present invention provides a process for preparing alkyl substituted aromatic compounds, including long chain alkyl substituted aromatic compounds, which comprises alkylating an aromatic compound with an alkylating agent possessing an alkylating aliphatic group having at least six carbon atoms under alkylation reaction conditions

in the presence of an alkylation catalyst comprising a porous, crystalline zeolite which has been selectively dealuminated, under acidic conditions, to remove non-framework aluminum. Additionally, the present invention provides a catalyst comprising a USY zeolite having a unit cell size from about 2.440 to about 2.464 nm and a bulk silica:alumina ratio of about 6.5 to about 10.0, wherein the non-framework aluminum content ranges from about 0 to about 25% of the total aluminum content.

Detailed Description

The starting materials for the production of the alkylated aromatic compounds include the aromatic compounds themselves. The term "aromatic compound" is understood by those of ordinary skill in the art to refer to any compound having at least one aromatic ring, including, but not limited to, benzene, pyridine, naphthalene. The aromatic compound may be unsubstituted or substituted with, by way of non-limiting examples, halogen, alkyl, alkenyl, nitro, amino, amido, carboxyl, carboxamido, etc. Naphthalenes include naphthalene itself as well the substituted naphthalenes which may contain, for example, one or more short chain alkyl groups containing up to about eight carbon atoms, such as methyl, ethyl or propyl. Suitable alkyl-substituted naphthalenes include, for example, alpha-methylnaphthalene, dimethylnaphthalene and ethylnaphthalene. Naphthalene itself is preferred since the resulting mono-alkylated products have better thermal and oxidative stability than the more highly alkylated materials for the reasons set forth above.

Various other aromatic chemical compounds containing one or two aromatic rings in the structure can also be alkylated by this process. Such compounds include, but are not limited to, alkylbenzenes such as benzene, toluene, xylenes, ethyl benzene, methylethyl benzene, trimethyl benzene, and propyl benzene. Also included are other two-ring aromatic compounds such as, for example, diphenyl oxide, diphenyl sulfide, diphenyl methane, biphenyl, and alkyl-substituted derivative compounds.

The alkylating agents which are used to alkylate the naphthalene include, but are not limited to, any aliphatic or aromatic organic compound having one or more available alkylating aliphatic groups capable of alkylating the naphthalene. The alkylating group itself should have at least about 6 carbon atoms, preferably at least about 8, and still more preferably at least about 12 carbon atoms. For the production of functional fluids and additives, the alkyl groups on the alkyl-naphthalene preferably have from about 12 to about 30 carbon atoms, with particular preference to about 14 to about 18 carbon atoms. A preferred class of alkylating agents is olefins with the requisite number of carbon atoms, including, but not limited to, the hexenes, heptenes, octenes, nonenes, decenes, undecenes, dodecenes, tridecenes, tetradecenes, pentadecenes, hexadecenes, heptadecenes, and octadecenes. Mixtures of the olefins, e.g., mixtures of C_{12} -C_{20} or C_{14} -C_{18} olefins, are also useful. Branched alkylating agents, especially oligomerized olefins such as, for example, the trimers, tetramers, pentamers, etc., of light olefins including, but not limited to, ethylene, propylene, the butylenes, etc., are also useful. Other useful alkylating agents that may be used include alcohols (inclusive of monoalcohols, dialcohols, trialcohols, etc.) such as, for example, hexanols, heptanols, octanols, nonanols, decanols, undecanols, and dodecanols; and alkyl halides such as hexyl chlorides, octyl chlorides, dodecyl chlorides; and higher homologs.

The alkylation reaction between the naphthalene and the alkylating agent is carried out in the presence of a zeolite catalyst that contains a cation of certain specified radius. The molecular size of the alkylation

products will require a relatively large pore size in the zeolite in order for the products to leave the zeolite, indicating the need for a relatively large pore size in the zeolite, which will also tend to reduce diffusion limitations with the long chain alkylating agents. The large pore size zeolites are the most useful zeolite catalysts for this purpose, although the less highly constrained intermediate pore size zeolites may also be used, as discussed below. The large pore size zeolites include, but are not limited to, zeolites such as faujasite, the synthetic faujasites (zeolites X and Y), zeolite L, ZSM-4, ZSM-18, ZSM-20, MCM-68, mordenite, and offretite, which are generally useful for this purpose, are characterized by the presence of a 12-membered oxygen ring system in the molecular structure and by the existence of pores with a minimum dimension of at least 7.4 Å, as described by Frilette *et al.* in J. Catalysis 67, 218-222 (1981). See also Chen *et al.*, "Shape-Selective Catalysis in Industrial Applications," (Chemical Industries, Vol. 36) Marcel Dekker Inc., New York 1989, ISBN 0-8247-7856-1; and Hoelderich *et al.*, Agnew. Chem. Int. Ed. Engl. 27, 226-246 (1988), especially pp. 226-229. The large pore size zeolites may also be characterized by a "Constraint Index" of not more than about 2, in most cases not more than about 1. Zeolite beta, a zeolite having a structure characterized by twelve-membered pore openings, is included in this class of zeolites although under certain circumstances it has a Constraint Index approaching the upper limit of about 2 which is characteristic of this class of zeolites. The method for determining Constraint Index is described in U.S. Patent No. 4,016,218, together with values for typical zeolites and of the significance of the Index in U.S. Patent No. 4,861,932, to which reference is made for a description of the test procedure and its interpretation.

Zeolites whose structure is that of a ten-membered oxygen ring, generally regarded as the intermediate pore size zeolites, may also be effective catalysts for this alkylation reaction if their structure is not too highly constrained. Thus, zeolites such as ZSM-12 (Constraint Index 2) may also be effective catalysts for this reaction. The zeolite identified as

MCM-22 is a useful catalyst for this reaction. MCM-22 is described in WO 90/6283, to which reference is made for a description of this zeolite. Thus, zeolites having a CI up to about 3 will generally be useful catalysts, although the activity may be found to be dependent on the choice of alkylating agent, especially its chain length, a factor that imposes diffusion limitations upon the choice of zeolite. MCM-49 and MCM-56 are also useful catalysts according to the present invention.

A highly useful zeolite for the production of the monoalkylated naphthalenes is ultrastable Y, usually referred to as USY. When this material contains hydrated cations, it catalyses the alkylation in good yields with excellent selectivity. Zeolite USY is a material of commerce, available in large quantities as a catalyst for the cracking of petroleum. It is produced by the stabilization of zeolite Y by a procedure of repeated ammonium exchange and controlled steaming. Processes for the production of zeolite USY are described in U.S. Patent Nos. 3,402,966, 3,923,192 , and 3,449,070; see also Wojciechowski, "Catalytic Cracking, Catalysts, Chemistry and Kinetics," (Chemical Industries, Vol. 25), Marcel Dekker, New York, 1986, ISBN 0-8247-7503-8, to which reference is made for a description of zeolite USY, its preparation and properties.

It is preferred to use a small crystal Y zeolite, ranging from about 0.2 to about 0.4 micron, although materials ranging from about 0.6 to about 1.3 micron, which is more typical of Y zeolite crystals, may also be used.

The alkylation reaction conditions include a temperature ranging from about 100 °C to about 400 °C and a pressure of from about 0.2 to about 25 atmospheres and a weight hourly space velocity of from about 0.1 to about 10. The mole ratio of the alkylatable aromatic to alkylating agent ranges from about 0.1:1 to about 50:1.

According to one aspect of the invention, an aromatic compound alkylation catalyst is provided which comprises a USY zeolite having a unit

cell size from about 2.440 to about 2.464 nm, a bulk silica:alumina ratio of about 6.5 to about 10.0 and a non-framework aluminum content below about 25 percent of the bulk aluminum.

According to another aspect of the invention, an aromatic compound alkylation catalyst is provided which comprises a USY zeolite having a unit cell size from about 2.446 to about 2.460 nm, a bulk silica:alumina ratio of about 6.5 to about 9.0 and a non-framework aluminum content below about 25 percent of the bulk aluminum. In such a catalyst composition the molar ratio of nitrogen to protonic species is within the range of about 80:20 to about 20:80.

Example 1

Preparation of H^+/NH_4^+ USY Crystal Sample

A commercial Na-form USY with a silica-to-alumina ratio of 5.5 and a unit cell size of 24.54 ´ was used for this catalyst preparation. The Na-form USY was ammonium exchanged twice with 1 M ammonium sulfate solution at a pH of about pH 5.5 and washed with deionized water (10 cc/g zeolite). Then the wet USY zeolite was dried in an oven at 120 °C overnight. The material was air-calcined (5 cc air/g zeolite/min) for 3 hours at 350 °C to control the residual water and ammonia levels. The properties of USY are shown in Table 1.

Example 2

Preparation of Dealuminated H^+/NH_4^+ USY Crystal Sample

A commercial Na-form USY with a silica-to alumina ratio of 5.5 and a unit cell size of 24.54 ´ was used for this catalyst preparation. The Na-form USY was made into a slurry with deionized (DI) water to target a 35 wt% solids level. A solution of 30 wt% ammonium sulfate was prepared, and then the pH was adjusted to 4.0 using 20 wt% H_2SO_4 solution. The pH 4.0 ammonium sulfate solution was added slowly to the USY slurry (1.3 g of 30% ammonium sulfate solution per 1 g zeolite) while the overall solution pH was adjusted to 4.0. The exchanged USY zeolite was filtered

and washed with deionized water (10 cc/g zeolite) and then dried in an oven at 120 °C overnight. The material was air calcined (5 cc air/g zeolite/min) for 3 hours at 350 °C. The properties of the final catalyst are shown in Table 1.

Example 3

Preparation of Dealuminated H^+/NH_4^+ USY Crystal Sample

The preparation procedure for this example is nearly identical to Example 2, except that the exchange pH was 3.5. The properties of the final catalyst are shown in Table 1.

Example 4

Preparation of Dealuminated H^+/NH_4^+ USY Crystal Sample

The preparation procedure for this example is nearly identical to Examples 2 and 3, except that the exchange pH was 3.0. The properties of the final catalyst are shown in Table 1.

TABLE 1

Properties of H^+/NH_4^+ USY Crystal Samples

Description	Na^+ USY	H^+/NH_4^+ USY	H^+/NH_4^+ USY	H^+/NH_4^+ USY	H^+/NH_4^+ USY
Example No.	Starting USY	Example 1	Example 2	Example 3	Example 4
Exchange pH for NH_4^+ Exchange	-	5-6	4.0	3.5	3.0
Calcination Temp. °C	-	350	350	350	350
N, wt%	-	0.67	0.37	0.70	0.63
S, wt%	-	0.30	0.1	<0.06	<0.06
Ash, wt%	95.7	92.0	92.8	91.3	82.7
Surface area, m^2/g	808	829	740	808	861
Na, wt%	2.9	0.4	0.6	0.5	0.3
SiO_2, wt%	70.2	69.1	67.7	70.8	74.3
Al_2O_3, wt%	22.0	21.3	20.4	17.5	14.7
Bulk SiO_2/Al_2O_3 Ratio (molar)	5.4	5.5	5.6	6.9	8.6
Unit Cell Size, , by XRD	24.56, 24.54	24.54	24.54	24.52	24.48
SiO_2/Al_2O_3 Ratio (molar) by XRD(a)	7.0-7.6	7.6	7.6	8.1	9.6
SiO_2/Al_2O_3 Ratio (molar) by NMR (b)	8.8	-	8.8	9.1	9.7

(a): SiO_2/Al_2O_3 molar ratio calculated based on publication by D.W. Breck, "Zeolite Molecular Sieves, Structural Chemistry and Use," John Wiley Publisher, N.Y., p. 911 (1974). The Breck correlation was developed for Na^+ form USY. Application of the Breck correlation for the Na^+ H^+/NH_4^+ form USY may not give correct SiO_2/Al_2O_3 molar ratios, but the data clearly show a trend consistent with the ^{29}Si NMR results.

(b): SiO_2/Al_2O_3 molar ratio calculated from ^{29}Si NMR based on publication by E. Lippmaa, M. Maegi, A. Samoson, and G. Englehardt, J. Am. Chem. Soc., 103, p. 4992 (1981).

The results above show that an ammonium sulfate exchange at pH 3.5 or above removes some of the aluminum (Al) species in USY while the unit cell size is rather constant (varies only from 24.54 ´ to 24.52 ´). The constant unit cell size means that the framework SiO_2/Al_2O_3 molar ratio, e.g., framework Al content, is rather constant. The results suggest that we are selectively removing the non-framework Al in USY during the ammonium exchange at pH 3.5. The ammonium exchange at pH 3.0 removes not only the non-framework Al but also some of the framework Al.

The SiO_2/Al_2O_3 molar ratios determined by NMR also show that ammonium exchange at pH 3.5 selectively removes the non-framework Al, and at pH 3.0 both framework and non-framework Al are removed.

The extent of dealumination can be estimated as follows. For example, if we subject 100 g of Na^+-form USY (100% solids basis) to the exchanges in the above examples we can estimate the following yields of Na_2O and Al_2O_3 assuming the SiO_2 content in USY stays constant during the exchange (this assumption is reasonable since SiO_2 does not dissolve in an acidic solution). The following estimates were made using the bulk SiO_2/Al_2O_3 molar ratios determined by elemental analysis and the framework SiO_2/Al_2O_3 molar ratios determined by ^{29}Si NMR.

TABLE 2

Estimates of Framework and Non-Framework Al Dealumination of H^+/NH_4^+ USY Crystal Samples

Exchange pH	NaUSY Starting	pH 4 Exchange	pH 3.5 Exchange	pH 3.0 Exchange
	USY	Example 1	Example 2	Example 3
Total SiO_2, g	73.8	73.8	73.8	73.8
Total Na_2O, g	3.1	0.6	0.5	0.3
Total Al_2O_3, g	23.1	22.2	18.2	14.6
g Al_2O_3, from framework (a)	14.7	14.7	14.3	13.7
g Al_2O_3, from non-framework (b)	8.4	7.5	3.9	0.9
wt% dealumination from framework	base	0%	3%	7%
wt% dealumination from non-framework	base	11%	54%	89%

(a): All weights are based on a 100 g starting Na-USY at 100% solids basis. Ammonium exchange will cause some loss of Al_2O_3 and Na_2O, thus the total will be less than 100 g for the exchanged samples.

(b): The framework Al content is calculated from SiO_2/Al_2O_3 molar ratio determined by ^{29}Si NMR based on publication by E. Lipmaa, M. Maeigi, A. Samoson, and G. Englehardt, J. Am. Chem. Soc., 103, 4992 (1981).

(c): The non-framework Al content is an estimate, a difference between the total Al_2O_3 content and the Al_2O_3 content corresponding to framework Al.

Example 5

Catalytic evaluation of H^+/NH_4^+ USY Crystal Samples

Three H^+/NH_4^+ USY samples from Examples 2 through 4 were evaluated for alkylating naphthalene with a long chain alpha olefin to produce alkylated naphthalene lube base stocks. The alkylation experiment was carried out in a stirred vessel using 3.7 wt% of catalyst and 96.3 wt% of 1.2:1 molar ratio of alpha C16 olefin:naphthalene. The reactants in the vessel were then heated to 200 °C and held at the temperature for 2 hours, under nitrogen atmosphere. The total liquid product was then analyzed using gas chromatography to determine the amounts of unreacted naphthalene, olefin, monoalkylate and dialkylate. The results are summarized in Table 3.

TABLE 3

Catalyst Performance vs. Dealumination of H^+/NH_4^+ USY Crystal Samples

	Example 2	Example 3	Example 4
Exchange pH	pH 4.0	pH 3.5	pH 3.0
Naphthalene Conversion wt %	85.4	94.7	94.7
Total Lube yield, wt%	84.8	92.4	95.1
Product Distrib., wt %, Monoalkylated + Diolefins	77.7	85.8	79.8
Dialkylated	7.1	6.6	15.3
Unreacted Naphthalene	4.7	1.7	1.7
Unreacted Olefins	10.5	5.9	3.2

The results in Table 3 show that the exchange condition is one of the important variables in alkylated naphthalene catalyst performance. Ammonium sulfate exchange at pH 3.5 or below is preferred since it improves the naphthalene conversion by 9.3 wt% (85.4% to 94.7%) and the corresponding lube yield. It also lowers the content of unreacted starting materials at the end of the batch reaction, thus improving the recovery process of the unreacted reactants.

The catalyst performance of the above USY samples are related to dealumination of non-framework Al (so-called "junk Al") in USY as shown in Table 4. Ammonium exchange at pH 3.5 or below selectively removes the non-framework Al or other occluded debris in USY.

TABLE 4

Catalyst Performance vs. Dealumination of H^+/NH_4^+ USY Crystal Samples

Exchange pH	Conversion, wt% @ 200 °C	wt% dealumination from framework Al	wt% dealumination from non-framework Al
NaUSY	-	base	base
pH 4.0 exch	85.4	0	11
pH 3.5 exch	94.7	3	54
pH 3.0 exch	94.7	7	89

The advantage we observed with dealuminated USY may be due to elimination of occluded materials such as non-framework Al, trapped sulfates, and other debris. While not wishing to be bound by any theory, we believe that alkylation of naphthalene with a long chain alkyl olefin

inside USY crystals is hindered significantly by diffusion of the bulky molecules in a liquid phase. By eliminating occluded materials inside USY, the diffusion might be improved. As a result, the reactivity is enhanced. This is consistent with our observation that removal of non-framework Al, not the framework Al, is critical to increase the catalyst activity.

Example 6

Preparation and Evaluation of [H^+/NH_4^+] USY/Silica-Clay Spray Dried Catalysts

Ammonium exchanged USYs prepared by procedures described in Examples 2 and 3 were used for these catalyst preparations (Examples 6-1 and 6-2, respectively).

Ammonium exchanged USY was slurried and ball milled for 16 hours to produce <5 μ average particle size. A physical mixture of 40 parts milled USY slurry, 30 parts colloidal silica, and 30 parts kaolin clay was slurried to form a uniform mixture. All components were blended based on parts by weight on a 100% solids basis. Sufficient amount of deionized water was added to form a spray dryable mixture (approximately 32-34 wt% solids). The mixture was spray dried to fine spherical particles having a particle size of approximately 70 μ. The spray product was then air calcined for 3 hours at 400 °C. The properties of the final catalysts are shown in Table 5.

The [H^+/NH_4^+] USY/Silica-Clay catalysts were evaluated for alkylation reaction under identical conditions as in Example 5, except that the catalyst charge was 5%. The process results are summarized in Table 5.

TABLE 5

Properties and Performances of [H^+/NH_4^+] USY/Silica-Clay Catalysts

Effect of Ammonium Exchange pH (5.0 wt% Catalyst Charge)

	Example 6-1 [H^+/NH_4^+] USY/Silica-Clay	Example 6-2 [H^+/NH_4^+] USY/Silica-Clay
Catalyst Properties		
Exchange pH	4.0	3.5
Calcination Temp., °C	400	400
N, wt%	0.02	0.06
S, wt%	0.14	0.14
Ash, wt%	90.8	86.3
Na, wt%	0.4	-
Surface Area, m^2/g		
	-	273
Catalyst Performance		
Naphthalene Conv., wt%	80.5	89.2
Total Lube Yield, wt%	82.5	83.4
	Product Distrib., wt%	
Monoalkylated + Diolefins	58.6	68.1
Dialkylated	23.9	15.3
Unreacted Naphthalene	6.3	3.5
Unreacted Olefins	11.2	13.5

Results in Table 5 again show that the exchange pH affects the final catalyst activity significantly. An ammonium sulfate exchange at pH 3.5 or below is preferred since it improves the naphthalene conversion by 8.7 wt% (80.5% to 89.2%) and the corresponding mono-alkylate yield.

Example 7

Preparation and Evaluation of [H^+/NH_4^+] USY/Silica-Clay Spray Dried Catalysts

NH_4^+-form USY, which was ammonium exchanged at pH 3.5 per procedures described in Example 3, was used for this catalyst preparation. The ammonium exchanged USY was slurried and ball milled for 16 hours to produce <5 μ average particle size. A physical mixture of 75 parts milled USY slurry, 20 parts colloidal silica, and 5 parts kaolin clay was slurried to form a uniform mixture. All components were blended based on parts by weight on a 100% solids basis. Sufficient amount of deionized water was added to form a spray-dryable mixture (approximately 32-34

wt% solids). The mixture was spray dried to fine spherical particles with approximately 70 μ average particle size. The spray product was then divided into three samples and air calcined for 3 hours at 125 °C, 350 °C, and 538 °C, respectively. The properties of the final catalysts are shown in Table 6.

The above [H^+/NH_4^+] USY/Silica-Clay catalysts were evaluated for alkylation reaction under identical conditions as in Example 6, except that the catalyst charge was 3.7 wt%. The process results are summarized in Table 6.

TABLE 6

Properties and Performances of [H^+/NH_4^+] USY/Silica-Clay Catalysts

Effect of Calcination Temperature

(3.7 wt% Catalyst Charge)

	Example 7-1 [H^+/NH_4^+] USY/Silica-Clay	Example 7-2 [H^+/NH_4^+] USY/Silica-Clay	Example 7-3 [H^+/NH_4^+] USY/Silica-Clay
Catalyst Properties			
Exchange pH	3.5	3.5	3.5
Calcination Temp., °C	250	350	538
N, wt%	0.64	0.30	0.02
S, wt%	0.08	0.08	0.08
Surface Area, m^2/g	-	-	478
Catalyst Performance			
Naphthalene Conv., wt%	91.0	94.4	93.8
Total lube yield, wt%	85.8	95.3	93.9
	Product Distrib., wt%	**Product Distrib., wt%**	**Product Distrib., wt%**
Monoalkylated + Olefins	82.2	86.6	79.7
Dialkylated	3.6	8.7	14.2
Unreacted naphthalene	2.9	1.8	2.0
Unreacted olefins	11.3	2.9	4.1

This example shows that the catalyst activity and selectivity can be further varied by varying the H^+ to NH_4^+ ratio of the [H^+/NH_4^+] USY/Silica-Clay catalyst. By adjusting the calcination temperature, the residual N level was varied from about 0.64 wt% to about 0.02 wt%. As the catalyst contains more N, the catalyst tends to be less active and the selectivity toward monoalkylate reactant increases. These findings are consistent to

the earlier results reported by Ardito et a. (2). The range of preferred N levels is similar to what Ardito *et al.* claimed earlier, wherein the ratio of ammonium to protonic species is within the range of 80:20 to 20:80 molar ratio.

Example 8

Zeolite Loading Effect

Examples 6 and 7 contain catalysts with identical ingredients, but vastly different composition, particularly the zeolite content. As the zeolite content increases from about 40 wt% to about 75 wt%, the catalyst activity increases substantially. As shown in the table below, the catalyst activity comes mostly from USY in that the relative reactivity of the catalyst is proportional to the zeolite content.

	Example 6-2 40 wt% USY	Example 7-2 75 wt% USY
Catalyst Charge for Evaluation	5 wt%	3.7 wt%
Conversion @ 2 hrs.	89.2%	94.4%
USY Charge Ratio	1.0	1.39
Relative Reactivity	1.0	1.43

The high-zeolite, high activity USY containing catalyst has an advantage in commercial practice. After each batch reaction, the catalyst needs to be filtered out and discarded. By lowering the total catalyst charge per batch reaction (from about 5 wt% to about 3-3.7 wt%), the filtration step would take much less time and the catalyst disposal will cost less.

Example 9

Preparation and Evaluation of $[H^+/NH_4^+]$ USY/Silica-Clay Catalyst Using High Unit Cell Size USY

A commercial Na-form USY with a silica-to-alumina ratio of 5.5 and a unit cell size of 24.60 ´ was used for this catalyst preparation. The Na-form USY was ammonium exchanged at pH 3.5 per procedures described in Example 3. The ammonium exchanged USY was slurried and ball milled for 16 hours to produce <5 average particle size. A physical mixture

of 75 parts milled USY slurry, 20 parts colloidal silica, and 5 parts kaolin clay was slurried to form a uniform mixture. All components were blended based on parts by weight on a 100% solids basis. Sufficient amount of deionized water was added to form a spray dryable mixture (approximately 32-34 wt% solids). The mixture was spray dried to fine spherical particles with approximately 70 μ average particle size. The spray product was then air calcined for 3 hours at 350 °C. The properties of the final catalysts are shown in Table 7. The [H^+/NH_4^+] USY/Silica-Clay catalyst was evaluated for alkylation reaction under identical conditions as in Example 5, except that the catalyst charge was about 3.0 wt%. The performance results were compared with a catalyst prepared per procedure in Example 7-2.

TABLE 7

Properties and Performance of [H^+/NH_4^+] USY/Silica-Clay Catalysts

Effect of Unit Cell Size of Starting USY (3.0 wt% Catalyst Charge)

	Example 9 [H^+/NH_4^+] USY/Silica-Clay	Example 7-2 [H^+/NH_4^+] USY/Silica-Clay
Catalyst Properties		
Na-USY Unit Cell Size,	24.60	24.54
Calcination Temp., oC	350	350
N, wt%	0.34	0.65
S, wt%	0.11	0.07
Ash, wt%	81.0	94.9
Na, wt%	0.5	0.6
Surface Area, m^2/g	573	529
Catalyst Performance		
Naphthalene Conv. @ 2 hrs, wt%	93.4	88.2
Total lube yield, wt%	-	87.2
	Product Distrib., wt%	
Monoalkylated + Diolefins	-	78.4
Di-alkylated	8.4	8.8
Unreacted naphthalene	2.1	3.8
Unreacted olefins	-	9.0

The above example shows that the catalyst activity and selectivity can be varied by varying the unit cell size of the starting Na-USY crystals. By

using larger unit cell size USY crystals, we were able to increase the catalyst activity even further. This effect of unit cell size to the catalyst performance for alkylated naphthalene synthesis was not been observed by others before.

Example 10

Preparation of Alkyl Diphenyl Sulfides Using H^+/NH_4^+ USY Catalyst

A H^+/NH_4^+ USY catalyst was prepared per the following procedure. A commercial Na-form USY with a silica-to-alumina ratio of 5.9 and a unit cell size of 24.62 Å was used for this catalyst preparation. The Na-form USY was made into a slurry with water to target a 35 wt% solids level. A solution of 30 wt% ammonium sulfate was prepared. The ammonium sulfate solution was added slowly to the USY slurry (1.3 g of 30% ammonium sulfate solution per 1 g zeolite). Then the pH of the USY/ ammonium sulfate slurry was adjusted to 3.1 using 20 wt% H_2SO_4 solution while stirring. The exchanged USY zeolite was filtered and washed with water. Then the USY was exchanged one more time on a belt filter using an ammonium sulfate solution (solution pH of 2.0, 0.3 g of 30% ammonium sulfate solution per 1 g zeolite) followed by extensive washing and filtration. The filter cake was spray dried at 170 °C. Then the material was calcined in the atmosphere in a rotary calciner at 500°C. The properties of the final catalyst are as follows:

Unit Cell Size, Å	24.55
N, wt%	1.33
S, wt%	0.09
Ash, wt%	93.0
Na, wt%	0.32
Surface Area, m^2/g	849
SiO_2, wt%	81.1
Al_2O_3, wt%	16.7
Bulk SiO_2/Al_2O_3 Ratio (molar)	8.24
SiO_2/Al_2O_3 Ratio (molar) by NMR	8.7
Wt% of non-framework Al relative to the total bulk Al	5.3

The above H^+/NH_4^+ USY catalyst was evaluated for alkylation of diphenyl sulfide with a long chain alpha olefin to produce alkylated diphenyl sulfide lube base stock. 1-Hexadecene (224 g), diphenyl sulfide (186 g) and the H^+/NH_4^+ USY catalyst (13.4 g) were added to a reaction flask and heated to 220 °C under a nitrogen atmosphere. After five hours, the reaction mass was cooled and the catalyst removed by filtering through a bed of diatomaceous earth filter medium (Celite 545). The filtrate was then heated to 196 °C and unreacted material (68.2 g) was removed through distillation at 4-mm Hg absolute pressure. The final product contains 94% monoalkylate and 6% dialkylate and had the following physical properties:

40C KV, cSt	27.27
100C KV, cSt	4.871
Viscosity Index	100
Pour Point, °C	-42

The alkylated product exhibits favorable VI and pour point suggesting the material could be useful as functional fluid or additive for synthetic lube stock.

Example 11

Preparation of Alkyl Diphenyl Oxides Using $[H^+/NH_4^+]$ USY/ Silica-Alumina-Clay Catalyst

A $[H^+/NH_4^+]$ USY/ Silica-Alumina-Clay catalyst was prepared per following procedure. USY with a silica-to-alumina ratio of 5.5 and a unit cell size of 24.54 Å was ammonium exchanged at pH 3.2. The ammonium exchanged USY was slurried and ball milled for 16 hours to produce <5 μ average particle size. A physical mixture of 75 parts milled USY slurry, 16.7 parts colloidal silica, 3.3 parts formic acid peptized alumina, and 5 parts kaolin clay was slurried to form a uniform mixture. All components were blended based on parts by weight on a 100% solids basis. Sufficient amount of deionized water was added to form a spray dryable mixture

(approximately 32-34wt% solids). The mixture was spray dried to fine spherical particles with approximately 70 μ average particle size. The spray product was then air calcined for 3 hours at 350 °C.

The above catalyst was evaluated for alkylation of diphenyl oxide with a long chain alpha olefin to produce alkylated diphenyl oxide lube base stock. Diphenyl oxide (425 g), activated carbon (3.81 g) and the catalyst (19.0 g) were added to a reaction flask and heated to 200 °C under a nitrogen atmosphere. 1-Hexadecene (336 g) was added dropwise to the flask over two hours. After holding an additional 40 minutes, the reaction mass was cooled and the catalyst removed by filtering through a bed of diatomaceous earth filter medium (Celite 545). The filtrate was then heated to 240 °C and unreacted material was removed through distillation at 10-mm Hg absolute pressure. The final product (558 g) contained 97% monoalkylate and 3% dialkylate and had the following physical properties:

40C KV, cSt	23.29
100C KV, cSt	4.361
Viscosity Index	90
Pour Point, °C	-45

The alkylated product exhibits favorable VI and pour point suggesting the material could be useful as functional fluid or additive for synthetic lube stock.

Example 12

Preparation of Alkyl Biphenyls Using H^+/NH_4^+ USY Catalyst

The H^+/NH_4^+ USY catalyst from Example 10 was evaluated for alkylation of biphenyl with a long chain alpha olefin to produce alkylated biphenyl lube base stock. 1-Hexadecene (224 g), biphenyl (154 g) and the H^+/NH_4^+ USY catalyst (19.9 g) were added to a reaction flask and heated to 140 °C under a nitrogen atmosphere. After five hours, 81% of the reactants had been converted to alkylates and the reaction mass was

cooled and the catalyst removed by filtering through a bed of diatomaceous earth filter medium (Celite 545). The filtrate was then heated to 192 °C and unreacted material was removed through distillation at 4-mm Hg absolute pressure. The final product contains 96% monoalkylate and 4% dialkylate and had the following physical properties:

40C KV, cSt	32.17
100C KV, cSt	5.157
Viscosity Index	83
Pour Point, °C	-45

The alkylated product exhibits favorable VI and pour point suggesting the material could be useful as functional fluid or additive for synthetic lube stock.

Example 13

Preparation of Alkyl Diphenylmethanes Using H^+/NH_4^+ USY Catalyst

The H^+/NH_4^+ USY catalyst from Example 10 was evaluated for alkylation of diphenylmethane with a long chain alpha olefin to produce alkylated diphenylmethane lube base stock. 1-Hexadecene (224 g), diphenylmethane (168 g) and the H^+/NH_4^+ USY catalyst (20.7 g) were added to a reaction flask and heated to 200 °C under a nitrogen atmosphere. After five hours, 92% of the reactants had been converted to alkylates and the reaction mass was cooled and the catalyst removed by filtering through a bed of diatomaceous earth filter medium (Celite 545). The filtrate was then heated to 184 °C and unreacted material was removed through distillation at 4-mm Hg absolute pressure. The final product contains 95% monoalkylate and 5% dialkylate and had the following physical properties:

40C KV, cSt	21.47
100C KV, cSt	4.383
Viscosity Index	113
Pour Point, °C	-48

The alkylated product exhibits favorable VI and the pour point suggesting the material could be useful as functional fluid for synthetic lube stock.

CLAIMS:

1. A catalyst for an aromatic alkylation of long chain alpha-olefins, the catalyst comprising a USY zeolite having a unit cell size ranging from 2.440 to 2.464 nm, a bulk silica:alumina ratio of 6.5 to 10.0, and a non-framework aluminum content ranging from slightly above 0 to 25 percent of the total aluminum content, and wherein said catalyst has an ammonium to protonic species molar ratio ranging from 80:20 to 20:80.

2. A catalyst according to claim 1, wherein the unit cell size of said USY zeolite ranges from 2.446 nm to 2.460 nm.

3. A catalyst according to claim 2, wherein the bulk silica:alumina ratio ranges from 6.5 to 9.0.