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

**(19) World Intellectual Property Organization**
International Bureau

**(43) International Publication Date**
**19 February 2009 (19.02.2009)**

**PCT**

**(10) International Publication Number**
**WO 2009/021727 A1**

**(51) International Patent Classification:**
***C07C 1/20*** (2006.01) ***B01J 29/40*** (2006.01)
***B01J 29/06*** (2006.01)

**(21) International Application Number:**
PCT/EP2008/006659

**(22) International Filing Date:** 13 August 2008 (13.08.2008)

**(25) Filing Language:** English

**(26) Publication Language:** English

**(30) Priority Data:**
07015872.0 13 August 2007 (13.08.2007) EP

**(71) Applicant** *(for all designated States except US)*: **SAUDI BASIC INDUSTRIES CORPORATION** [SA/SA]; P.O. Box 5101, Riyadh, 11422 (SA).

**(72) Inventors; and**
**(75) Inventors/Applicants** *(for US only)*: **KARIM, Khalid** [GB/SA]; Sabic Headquarters, Patent Section, P.O. Box 5101, 11422 Riyadh (SA). **AL-OTAIBI, Naif** [SA/SA]; Sabic Headquarters, Patent Section, P.O. Box 5101, 11422 Riyadh (SA). **ZAHEER, Syed** [IN/SA]; Sabic Headquarters, Patent Section, P.O. Box 5101, 11422 Riyadh (SA). **AL-SHABNAN, Abdulkareem** [SA/SA]; Sabic Headquarters, Patent Section, P.O. Box 5101, 11422 Riyadh (SA).

**(74) Agent: BOOTSMA, J., P., C.**; Sabic Corporate Patent Group, P.O. Box 3008, NL-6160 GA Geleen (NL).

**(81) Designated States** *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

**(84) Designated States** *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, NO, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

**Published:**
- — *with international search report*
- — *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

# (54) Title: CATALYST COMPOSITION AND PROCESS FOR CONVERTING ALIPHATIC OXYGENATES TO AROMATICS

**(57) Abstract:** The invention relates to a catalyst composition La-M/zeolite, which consists essentially of from 0.0001 to 20 mass % of La (lanthanum); from 0.0001 to 20 mass % of at least one element M selected from the group consisting of molybdenum (Mo), cerium (Ce) and caesium (Cs); a zeolite of the 10-ring structure type; and optionally a binder (mass% based on total catalyst composition). The invention also relates to the use of the catalyst composition according to the invention in various reactions, for examples in making aromatics from aliphatic hydrocarbons or oxygenated hydrocarbons with good selectivity and activity. The invention further relates more specifically to a process for converting a feed stream comprising oxygenated lower aliphatic hydrocarbon compounds, especially methanol, to a product stream comprising aromatic hydrocarbons and olefins, especially BTX, which process comprises a step of contacting said feed with the catalyst composition according to the invention.

# CATALYST COMPOSITION AND PROCESS FOR CONVERTING ALIPHATIC OXYGENATES TO AROMATICS

The invention relates to a catalyst composition comprising a lanthanum-containing zeolite. The invention also relates to the use of the catalyst composition according to the invention in various reactions, for example in making aromatics from oxygenated aliphatic hydrocarbons. The invention further relates to a process for converting a feed stream comprising oxygenated lower aliphatic hydrocarbon compounds to a product stream comprising aromatic hydrocarbons, which process comprises a step of contacting said feed with the catalyst composition according to the invention.

More specifically, the invention relates to a catalyst composition and a process for converting a feed stream comprising C1-C4 oxygenates to a product stream comprising C6-C8 aromatics.

Such a catalyst composition is known from patent publication US 4156698, wherein a feed comprising C1-C4 monohydric alcohol is converted to a mixture of aliphatic and aromatic hydrocarbons by contacting said feed with a composite catalyst consisting of a crystalline aluminosilicate zeolite, for example ZSM-5, and an aluminium matrix, modified with a mixture of rare earth metals, including lanthanum (La). A catalyst composition based on ZSM-5/alumina and containing 0.26 mass% of La is used to convert a methanol feed into gasoline boiling range hydrocarbons. Rare-earth modification of the alumina matrix would reduce decomposition of alcohol into carbon monoxide and hydrogen, and increase conversion to aromatics.

Aromatic hydrocarbon compounds like benzene, toluene and xylenes, together often referred to as BTX, are important building blocks in nowadays petrochemical industries. The general source of these compounds traditionally is refining of petroleum. Given the limitations in fossil petroleum resources, alternative sources for these aromatics are being developed.

Aliphatic oxygenates, which can be obtained from various carbon sources via for example synthesis gas, can be converted into a mixture containing aromatics like BTX; for which reaction various catalysts have already been proposed. For example, in US 3894103 aromatisation of a lower oxygenate compound like methanol by contacting with a crystalline aluminosilicate zeolite of specific constraint index and Si/Al ratio is described.

In US 4724270 it is taught that in the conversion of methanol to hydrocarbon the selectivity to aromatics improves if the acidity of the crystalline aluminosilicate zeolite of specific constraint index and Si/Al ratio of at least 12 is reduced by a thermal treatment of said catalyst.

US 4822939 teaches to use a Ga-containing ZSM-5 type zeolite, having a Si/Al ratio of 5000-35000 before Ga-exchange, to catalytically convert C1-C4 aliphatic oxygenates into C2-C5 olefins with improved yields and reduced formation of C1-C5 paraffin. It is indicated that at least part of the Ga should be present in the zeolite framework in tetrahedral coordination to provide Brönsted acid sites, and the zeolite should be substantially free of aluminium in the framework.

In WO 03/089135 a pentasil-type aluminosilicate containing sodium, zinc and a mixture of rare-earth metals including La is disclosed; this catalyst is used to make a mixture comprising liquid hydrocarbons from lower aliphatic hydrocarbon oxygenates. Advantage of said catalyst is indicated to be high yield of high-octane hydrocarbons with a low aromatics content.

A steamed La-modified ZSM-5/silica/kaolin catalyst composition is disclosed in WO 99/51549. This catalyst is used to make a mixture comprising C2-C4 olefins from methanol; but showed only 2% methanol conversion.

A La-Cu/ZSM-5 composition is disclosed in US 6126912, and used as catalyst for reducing $NO_x$ to $NO_2$.

US 5866741 discloses a La-Mo/betazeolite composition, which is applied as catalyst in converting C9+ aromatics into C6-C8 aromatics.

In WO 20005/080532 a La-Mo-Zn/Y-zeolite composition is disclosed, and shown to be useful as catalyst for converting C6+ hydrocarbons into linear C1-C5 alkanes.

There is a constant need in industry for catalysts and processes with improved performance in terms of overall process economics, and it is an object of the present invention to provide a new catalyst composition, which catalyst can for example be applied in a process for converting a feed stream comprising oxygenated lower aliphatic hydrocarbon compounds to a product stream comprising relatively high amounts of aromatic hydrocarbons, especially BTX.

This object is achieved according to the invention with a catalyst composition La-M/zeolite, which consists essentially of from 0.0001 to 20 mass% of La (lanthanum); from 0.0001 to 20 mass% of at least one element M selected from the group consisting of molybdenum (Mo), cerium (Ce) and caesium (Cs); a zeolite of the 10-ring structure type; and optionally a binder (mass% based on total catalyst composition).

The catalyst composition according to the invention surprisingly shows high productivity in combination with good selectivity in converting a feed stream comprising oxygenated lower aliphatic hydrocarbon compounds to a product stream comprising aromatic hydrocarbons. The catalyst also has the ability to convert aliphatics or mixtures of methanol and hydrocarbons to aromatics with a surprisingly high productivity and selectivity. The catalyst composition also has a lower cost in terms of metals used to modify zeolite.

Within the context of the present invention a zeolite, as comprised in the catalyst composition, is understood to mean an aluminosilicate, an aluminophosphate (AlPO) or a silicoaluminophosphate (SAPO). These inorganic porous materials are well known to the skilled man. An overview of their characteristics is for example provided by the chapter on Molecular Sieves in Kirk-Othmer Encyclopedia of Chemical Technology, Volume 16, p 811-853; in Atlas of Zeolite Framework Types, 5th edition, (Elsevier, 2001), and also by above-cited patent publications. The zeolite in the catalyst composition according to the invention is a crystalline material with homogeneous pore size and channelling framework structures, and its pores or channels are characterized by a 10-ring structure. Such zeolites are also referred to as medium pore size zeolites, with pore dimensions in the range of from 5 to 7 Å. Zeolites of the 12-ring structure type, like for example betazeolite, are also referred to as large pore sized; and those of the 8-ring structure type are called small pore size zeolites. In the above cited Altlas of Zeolite Framework Types various zeolites are listed based on ring structure.

Preferably, the zeolite is in the so-called hydrogen form, meaning that its sodium or potassium content is very low, preferably below 0.1, 0.05, 0.02 or 0.01 mass%; more preferably presence of sodium is below detection limits.

Preferably, the zeolite in the catalyst composition according to the invention is aluminosilicate. Any aluminosilicate that shows activity in converting aliphatic oxygenates to aromatics, before modifying with the specific metals of the invention, may be applied. Aluminosilicate zeolites can be characterized by the Si/Al ratio of the framework. This ratio may vary widely in the catalyst composition according to the invention. Preferably, the Si/Al ratio is from about 5 to 1000, more preferably from about 8 to 500, or from 10 to 300. Examples of suitable materials include the ZSM-series, or mixtures thereof. Preferred materials are those known as ZSM-5, ZSM-11, ZSM-23, ZSM-48 and ZSM-57.

Also aluminophosphates of medium pore size can be used as zeolite, like AlPO-11 or AlPO-41 are used.

In another preferred embodiment, the zeolite in the catalyst composition used in the process of the invention is a silicoaluminophosphate (SAPO). SAPO materials have properties of both aluminosilicates and aluminophopsphates. Any SAPO of medium pore size that shows activity in converting aliphatic oxygenates to aromatics, before modifying with the specific metals of the invention, may be applied.

The catalyst composition according to the invention consists essentially of a specific zeolite containing 0.0001-20 mass% of lanthanum (La), based on total catalyst composition. A certain minimum amount of lanthanum is needed to improve selectivity of the catalyst to form aromatics from aliphatic oxygenates; preferably the catalyst contains therefore at least 0.001, 0.005, 0.01, 0.05, 0.1, 0.2, 0.5, or even 1 mass% of La. If the zeolite would contain too high an amount of metal, the pores of the zeolite might become at least partly clogged, resulting in a masking effect. The La-content of the catalyst thus preferably at most 15, 10, 8, 6, 5, or even at most 4 mass%.

The catalyst composition according to the invention consists essentially of a specific zeolite containing 0.0001-20 mass% of lanthanum (La) and from 0.0001 to 20 mass% of at least one element M selected from the group consisting of molybdenum (Mo), cerium (Ce) and caesium (Cs), based on total catalyst composition. Presence of one or more of these elements is found to increase aromatics production from aliphatic oxygenates. Therefore, the catalyst preferably contains at least 0.001, 0.005, 0.01, 0.05, 0.1, 0.2, 0.5, or even at least 1 mass% of said elements; but at most 15, 10, 8, 6, or 5 mass%.

The La-M/zeolite catalyst composition according to the invention preferably contains at least two elements selected from the group consisting of Mo, Ce, and Cs, to further improve performance in for example methanol conversion to aromatics.

In a further preferred embodiment, the La-M/zeolite catalyst composition according to the present invention further contains copper (Cu) and/or Zinc (Zn) as (a) further element(s) in addition to the elements M as defined herein; both elements may be present in the same amounts as indicated above for La and the at least one element M. Such preferred catalysts according to the invention include La-Mo-Zn/zeolite and La-Mo-Cu-Zn/zeolite.

Preferably, total metal content of the La-M/zeolite composition according to the invention is from 0.1 to 25 mass%, or from 0.2 to 20 mass%.

The various metal elements contained in the catalyst according to the invention may be present in the zeolite structure as framework or non-framework elements; as counterions in the zeolite; on its surface, e.g. in the form of metal oxides; or be present in a combination of these forms.

The catalyst composition La-M/zeolite according to the invention as described above can optionally contain a binder; that is a component that does not negatively affect its catalytic performance, but mainly serves to provide physical integrity and mechanical strength to the catalyst particles. A binder may comprise a support or filler, mainly intended to dilute catalyst activity; and also binder material, which serves as a glue to hold the components together; both functions may also be combined in one material. Such binder is known to a skilled person. Examples of suitable materials include aluminas, silicas, clays such as kaolin, or combinations thereof. Preferably the binder, if used, is silica.

The catalyst composition according to the invention can be prepared by suitable methods of preparing and modifying zeolites as well known to the skilled person; including for example impregnation, calcination, steam and/or other thermal treatment steps.

If the catalyst composition in addition to the modified zeolite is to contain a binder, such composition can for example be obtained by mixing the modified zeolite and a binder in a liquid, and forming the mixture into shapes, like pellets or tablets, applying methods known to the skilled person.

The invention also relates to the use of the catalyst composition according to the invention as a catalyst in various chemical reactions, for example in making aromatic hydrocarbons from aliphatic hydrocarbons and/or oxygenated hydrocarbons.

The invention further relates more specifically to a process for converting a feed stream comprising oxygenated C1-C10 aliphatic hydrocarbon compounds to a product stream comprising aromatic hydrocarbons, which process comprises a step of contacting said feed with the catalyst composition according to the invention.

In the process according to the invention any hydrocarbon feedstock which comprises oxygenated lower aliphatic hydrocarbon compounds can be used as feed stream. Oxygenated hydrocarbon compounds are herein defined to include hydrocarbons containing aliphatic moieties and at least one oxygen atom, such as alcohols; ethers; carbonyl compounds like aldehydes, ketones, carboxylic acids.

Preferably, the oxygenated hydrocarbon compounds contain 1 to about 4 carbon atoms. Suitable oxygenated hydrocarbons include straight or branched chain alcohols, and their unsaturated analogues. Examples of such compounds include methanol, ethanol, iso-propanol, n-propanol, dimethyl ether, diethyl ether, methyl ethyl ether, formaldehyde, dimethyl ketone, acetic acid, and their mixtures.

Preferably, the feed stream in the process according to the invention comprises C1-C4 alcohols and/or their derivatives, more preferably the feed comprises methanol and/or its derivatives, like a methanol/dimethyl ether mixture.

The feed stream may further contain one or more diluents, the concentration of which may vary over wide ranges; preferably diluents form about 10-90 vol% of the feed. Examples of suitable diluents include helium, nitrogen, carbon dioxide, and water.

The feed stream may also contain other non-aromatic hydrocarbons, like paraffins and/or olefins; especially C1-C5 hydrocarbons. In a preferred way of performing the process according to the invention, the feed stream contains aliphatic hydrocarbons that are recycled from the product stream, for example after removing aromatic components, and which are then for example mixed with an oxygenates containing stream before contacting with the catalyst composition. The advantage hereof is that a higher conversion to aromatics is obtained, because the catalyst of the invention is also active for converting paraffins and olefins to aromatics.

The step of contacting the feed stream with the catalyst composition can be performed in any suitable reactor, as known to a skilled man, for example in a fixed bed, a fluidized bed, or any other circulating or moving bed reactor.

The contacting step may be performed at a temperature range of about 250 to 750 °C. A higher temperature generally enhances conversion to aromatics, the temperature is therefore preferably at least about 300, 350, or 400 °C. Because higher temperatures may induce side-reactions or promote deactivation of the catalyst, the temperature is preferably at most about 700, 600, or 550 °C. The reaction temperature preferably ranges between 400 to 550 °C.

Suitable pressures to conduct the contacting step are from about atmospheric to 3 MPa, preferably pressure is below about 2.5, 2.0, 1.5, 1.0 or even below 0.5 MPa.

The flow rate at which the feed stream is fed to the reactor may vary widely, but is preferably such that a weight hourly space velocity (WHSV) results of about 0.1 – 500 $h^{-1}$, more preferably WHSV is about 0.5 -250 $h^{-1}$, or 1 – 100 $h^{-1}$. WHSV is the ratio of the rate at which the feed stream is fed to the reactor (in weight or mass per hour) divided by the weight of catalyst composition in said reactor; and is thus inversely related to contact time.

The product stream in the process according to the invention comprises aromatic hydrocarbons, in addition to saturated and unsaturated aliphatic hydrocarbons, and optionally non-converted oxygenates.

In a preferred way of operating the process according to the invention, yield of aromatics is further increased by feeding the product stream to a subsequent second reaction step, wherein the reaction mixture made is contacted with a further catalyst composition to increase the contents of aromatics, for example by catalytically converting aliphatic hydrocarbons, especially olefins, present in the product stream. Suitable further catalysts include the catalyst composition of the invention, and any aromatization catalyst mentioned in the prior art.

The invention will now be further illustrated with below described experiments.

**Comparative experiment A**

Aluminosilicate ZSM-5 (from Zeolists) was calcined at 550 °C. Catalyst particles of 40-60 mesh size were loaded into a tubular fixed bed reactor for the conversion of methanol. The reaction was conducted at a temperature of 450 °C and pressure of 1 atmosphere at a weight hourly space velocity (WHSV) of 9 $h^{-1}$ with respect to methanol feed. Product stream composition was analysed by standard GC techniques. The results are summarized in Table 1.

Catalyst activity is measured as the amount of liquid organic compounds formed per hour; the amount of liquid organics being a measure for the amount of aromatic compounds formed. Further in Table 1 TMB means trimethylbenzenes; Σ BTX is defined as the mass% of the total BTX in the product divided by the methanol conversion (in mass%) and multiplied by 100; Σ Xylene is mass% of the total xylenes (m,p,o) in the product divided by methanol conversion (in mass%), multiplied by 100.

**Comparative experiment B**

ZSM-5 ( 65%) and alumina $Al_2O_3$ ( 35 %) were mixed in water and impregnated with mixture of 1.1 % $Re_2O_3$ and dried at 120°C overnight, and then calcined at

550°C. Catalyst in 40-60 mesh size was loaded into tubular fixed bed reactor for the conversion of methanol. The reaction was conducted at a temperature of 450°C and pressure of 1 atmosphere at weight hour space velocity (WHSV) of 9 with respect to methanol feed. The results of test runs are given in table.1

**Comparative experiment C**

A catalyst was prepared by ion-exchange and thermal treatment of commercially available ZSM-5 aluminosilicate (from Zeolists), with the desired amount of metals and following known procedures. 0.6 g of lanthanum nitrate (from Fluka) was dissolved in 100 g of distilled water and heated at 60-65 °C with continuous stirring. 10 g of ZSM-5 was added to the lanthanum nitrate solution and heated at 85 °C for 8 hours in a closed vessel (about 2 mass% of La added to ZSM-5); then the material was filtered and washed with 2 litres of hot water. The resultant catalyst slurry was dried in a closed oven at 120 °C for 16 hrs. The dried material was subsequently calcined in a rotary furnace with 1 °C temperature increase per minute to 450 °C, and held at that temperature for 6 hrs.

Catalyst of particle size 40-60 mesh was loaded into a tubular fixed bed reactor for the conversion of methanol. The reaction was conducted at a temperature of 450 °C and pressure of 1 atmosphere at a weight hourly space velocity (WHSV) of 9 $h^{-1}$ with respect to methanol feed; results are given in Table 1.

**Comparative experiment D**

Catalyst was prepared as in Comparative experiment C, but now 5 g of lanthanum nitrate was dissolved in 100 g of distilled water; resulting in about 16 mass% of La added to ZSM-5.

Methanol conversion reaction was performed as in Comparative experiment C; results are given in Table 1.

**Comparative experiment E**

Analogously to CE C a La-modified catalyst was prepared starting from a commercially available beta-zeolite (from Zeolists).

Dried and calcined catalyst of 40-60 mesh size and containing about 2 mass% of La was used for conversion of methanol, analogous to Comparative experiment C. Table 1 summarizes the results.

**Comparative experiment F**

A gallium-containing zeolite catalyst was prepared, following the procedure of US 4822939, by first calcining ZSM-5 (from Zeolists) at 538 °C. Then 4 g of calcined ZSM-5, 8 g of gallium nitrate in hydrated form, and 60 g of water were put in a teflon bottle, and heated to 150 °C for 18 hours. The resultant product was washed and changed into ammonium form, followed by calcination in air.

Catalyst in 40-60 mesh size was loaded into a tubular fixed bed reactor for the conversion of methanol. The reaction was conducted as in Comparative experiment C, and results are summarized in Table1.

**Example 1**

Analogous to CE C a modified ZSM-5 catalyst was prepared, applying 0.6 g of lanthanum nitrate dissolved in 100 g of distilled water; and 0.5 g of molybdenum oxide, 0.06 g of zinc oxide and 2.6 g of cupric nitrate trihydrated dissolved in 100g of water at 85 °C. Both solutions were mixed and 10 g of ZSM-5 was added to this solution and heated at 85 °C for 8 hours in a closed vessel; resulting in about 2 mass% La, 3 mass% Mo, 0.5 mass% of Zn and 7 mass% of Cu being added to ZSM-5.

Dried and calcined catalyst was used for conversion of methanol, analogous to Comparative experiments C and D. Table 1 shows a marked improvement in productivity and BTX selectivity.

**Example 2**

Catalyst was prepared by ion exchange and thermal treatment of the commercial available ZSM-5 from Zeolists with the desired amount of metals. 0.6 g of lanthanum Nitrate (fluka) was dissolved in 100g of distilled water and heated at 60-65°C on with continuous stirring. 0.5 g of molybdenum oxide and 0.06 g of zinc oxide were dissolved into 100g of water at 85°C at Ph 5. Both solutions were mixed and 10 g of ZSM-5 was added to this solution and heated at 85°C for 8 hours in a closed vessel. This represents about La (2%), Mo (3%), and Zn (0.5%) added to ZSM-5. Resultant catalyst was filtered and washed with 3 litres of hot water. The resultant catalyst slurry was dried in a closed oven at 120°C for 16 hrs. The dried catalyst was calcined in rotary furnace with 1°C temperature increase per minute till 450°C and held at 450°C for 6 hrs.

Catalyst in 40-60 mesh size was loaded into tubular fixed bed reactor for the conversion of methanol. The reaction was conducted at a temperature of 450°C and pressure of 1 atmosphere at weight hour space velocity (WHSV) of 9 with respect to methanol feed. The results of test runs are given in table 1.

**Example 3**

Analogous to Comparative experiment C a catalyst was prepared by ion exchange and thermal treatment of ZSM-5 (from Zeolists) with 0.6 g of lanthanum nitrate dissolved in 100 g of distilled water, and 0.5 g of molybdenum oxide dissolved in 100 g of water; resulting in about 2 mass% of La and 3 mass% of Mo in ZSM-5.
Dried and calcined catalyst of 40-60 mesh size was used for conversion of methanol, analogous to Comparative experiment C. Table 1 summarizes the results.

**Example 4**

Analogous to Comparative experiment C a catalyst was prepared by ion exchange and thermal treatment of ZSM-5 (from Zeolists) with 0.6 g of lanthanum nitrate dissolved in 100 g of distilled water, and 0.7 g of cesium nitrate dissolved in 100 g of water; resulting in about 2 mass% of La and 4.5 mass% of Cs in ZSM-5.
Dried and calcined catalyst of 40-60 mesh size was used for conversion of methanol, analogous to Comparative experiment C. Table 1 shows a marked improvement in productivity and BTX selectivity.

**Comparative experiment G**

Comparative experiment C was repeated, but now a mixed feed consisting of methanol/ethylene/propylene/N2 (36:7.7:6.3:50) is reacted over the catalyst at 450 °C and 1 atm, with a total flow of 65 cc/min . The results are presented in Table 2.

**Comparative experiment H**

Comparative experiment F was repeated, but now a feed consisting of methanol/ethylene/propylene/N2 mixture (36:7.7:6.3:50) is reacted over the catalyst at 450 °C and 1 atm, and with a total flow of 65 cc/min. Results are given in Table 2.

**Example 5**

Example 2 was repeated, but now a feed consisting of a methanol/ethylene/propylene/N2 mixture (36:7.7:6.3:50) is reacted over the catalyst at 450 °C and 1 atm, and with a total flow of 65 cc/min. Results are given in Table 2, and show a significant improvement in productivity and aromatics selectivity over La-modified zeolite and Ga-modified zeolite (CE G and H).

**Table 1**

| Experiment | Methanol Conversion | Productivity (liquid organics) | increment in productivity relative to Comparative experiment B | Σ BTX | Σ Xylenes | Σ Aromatics (total) | TMB | increment in Σ BTX relative to Comparative experiment B | increment in Σ Xylenes relative to Comparative experiment B | increment in Σ Aromatics relative to Comparative experiment B |
|---|---|---|---|---|---|---|---|---|---|---|
|  | wt% | g/hr | % | wt% | wt% | wt% | wt% | % | % | % |
| Comparative experiment A | 100 | 1 | 33 | 5.95 | 3.19 | 8.69 | 0 | 42 | 25 | 34 |
| Comparative experiment B | 95 | 0.75 | base | 4.2 | 2.55 | 6.50 | 0 | base | base | base |
| Comparative experiment C | 100 | 1.23 | 64 | 8.64 | 4.65 | 11.75 | 1.02 | 45 | 82 | 81 |
| Comparative experiment D | 100 | 0.83 | 10 | 7.13 | 3.68 | 9.85 | 0.27 | 20 | 44 | 52 |
| Comparative experiment E | 100 | 0.43 | -57 | 9.01 | 5.11 | 13.0 | 0.31 | 52 | 100 | 100 |
| Comparative experiment F | 100 | 0.93 | 31 | 7.16 | 3.61 | 8.90 | 0.77 | 20 | 42 | 37 |
| Example 1 | 100 | 1.35 | 80 | 10.15 | 5.52 | 13.4 | 1.83 | 71 | 116 | 106 |
| Example 2 | 100 | 1.86 | 148 | 13.77 | 7.98 | 18.8 | 2.31 | 103 | 212 | 189 |
| Example 3 | 100 | 1.07 | 42 | 7.27 | 4.14 | 9.85 | 1.25 | 22 | 62 | 52 |
| Example 4 | 100 | 1.32 | 76 | 10.63 | 5.52 | 12.88 | 1.03 | 78 | 116 | 98 |

**Table 2**

| Experiment | Methanol Conversion | Productivity (liquid organics) | increment in productivity relative to Comparative experiment H | Σ BTX | Σ Xylenes | Σ Aromatics | TMB | increment in Σ BTX relative to Comparative experiment H | increment in Σ Xylenes relative to Comparative experiment H | increment in Σ Aromatics relative to Comparative experiment H |
|---|---|---|---|---|---|---|---|---|---|---|
| | wt% | g/hr | % | wt% | wt% | wt% | wt% | % | % | % |
| Comparative experiment G | 100 | 0.56 | 72 | 16.36 | 8.3 | 21.58 | 1.75 | 71 | 83 | 129 |
| Comparative experiment H | 100 | 0.32 | base | 9.54 | 4.54 | 12.41 | 0.76 | base | base | base |
| Example 5 | 100 | 1.26 | 287 | 38.92 | 17.76 | 48.8 | 2.79 | 307 | 291 | 293 |

# CLAIMS

1. Catalyst composition La-M/zeolite, which consists essentially of from 0.0001 to 20 mass% of La (lanthanum); from 0.0001 to 20 mass% of at least one element M selected from the group consisting of molybdenum (Mo), cerium (Ce) and caesium (Cs); a zeolite of the 10-ring structure type; and optionally a binder (mass% based on total catalyst composition).
2. Catalyst composition according to claim 1, wherein the zeolite is a crystalline aluminosilicate.
3. Catalyst composition according to claim 2, wherein the aluminosilicate is selected from the group consisting of ZSM-5, ZSM-11, ZSM-23, ZSM-48 and ZSM-57.
4. Catalyst composition according to any one of claims 1-3, containing 0.01 - 10 mass% of La.
5. Catalyst composition according to any one of claims 1-4, containing 0.01 - 10 mass % of at least one element M selected from the group consisting of Mo, Ce or Cs.
6. Catalyst composition according to any one of claims 1-5, containing at least two elements selected from the group consisting of Mo, Ce, and Cs.
7. Catalyst composition according to any one of claims 1-6, further containing copper (Cu) and/or Zinc (Zn).
8. Process for converting a feed stream comprising oxygenated C1-C10 aliphatic hydrocarbon compounds to a product stream comprising aromatic hydrocarbons, which process comprises a step of contacting said feed with the catalyst composition according to any one of claims 1-7.
9. Process according to claim 8, wherein the feed stream comprises C1-C4 alcohols and/or their derivatives.
10. Process according to claim 8, wherein the feed stream comprises methanol and/or its derivatives.

11. Process according to any one of claims 8-10, wherein the feed stream further comprises C1-C5 hydrocarbons.
12. Process according to any one of claims 8-11, wherein temperature is from 250 to 750 °C, pressure is from atmospheric to 3 MPa, and WHSV is from 0.1 to 500 $h^{-1}$.

# INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2008/006659

**A. CLASSIFICATION OF SUBJECT MATTER**
INV. C07C1/20 B01J29/06 B01J29/40

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)
C07C B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X | US 4 156 698 A (DWYER FRANCIS G [US] ET AL) 29 May 1979 (1979-05-29)<br>cited in the application<br>example 2<br>claims 1,2,4-6,8,9<br>column 2, lines 17-21,31-46,58-63<br>column 3, lines 36-54<br>column 4, lines 3-5,20-26; table<br>----- | 1-5,8-12 |
| X | DATABASE WPI Week 200381<br>Thomson Scientific, London, GB; AN 2003-877158<br>XP002475735<br>& WO 03/089135 A (BUREAU ANTICRISIS MEASURES ZAO) 30 October 2003 (2003-10-30)<br>abstract<br>-/-- | 1-5,7-12 |

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

| | |
|---|---|
| Date of the actual completion of the international search<br>2 December 2008 | Date of mailing of the international search report<br>11/12/2008 |
| Name and mailing address of the ISA/<br>European Patent Office, P.B. 5818 Patentlaan 2<br>NL – 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040,<br>Fax: (+31-70) 340-3016 | Authorized officer<br>Jourdan, Angelika |

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X | & WO 03/089135 A (ZAKRITOE AKCHIONERNOE OBSCHEST [RU]; AVTONOMNAYA NEKOMMERCHESKAYA O [R)<br>30 October 2003 (2003-10-30) | 1-5,7-12 |
| A | US 4 066 714 A (RODEWALD PAUL G)<br>3 January 1978 (1978-01-03)<br>the whole document<br>examples 3,6 | 1-12 |
| A | US 4 992 611 A (MORRISON ROGER A [US])<br>12 February 1991 (1991-02-12)<br>examples 8-10 | 1-12 |
| A | WO 03/074177 A (EXXONMOBIL CHEM PATENTS INC [US]) 12 September 2003 (2003-09-12)<br>the whole document | 1-12 |

# INTERNATIONAL SEARCH REPORT

**Information on patent family members**

International application No
PCT/EP2008/006659

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---|---|---|
| US 4156698 A | 29-05-1979 | DE 2818831 A1 | 16-11-1978 |
| | | DE 2857758 C2 | 22-01-1987 |
| WO 03089135 A | 30-10-2003 | AU 2002306421 A1 | 03-11-2003 |
| US 4066714 A | 03-01-1978 | AU 506185 B2 | 13-12-1979 |
| | | AU 1985476 A | 01-06-1978 |
| | | NZ 182431 A | 28-03-1979 |
| | | ZA 7606454 A | 28-06-1978 |
| US 4992611 A | 12-02-1991 | AU 5525390 A | 18-07-1991 |
| | | WO 9108997 A1 | 27-06-1991 |
| WO 03074177 A | 12-09-2003 | AU 2003212993 A1 | 16-09-2003 |
| | | AU 2003216248 A1 | 16-09-2003 |
| | | AU 2003225560 A1 | 16-09-2003 |
| | | BR 0308011 A | 04-01-2005 |
| | | CA 2477428 A1 | 12-09-2003 |
| | | CA 2477432 A1 | 12-09-2003 |
| | | CN 1638865 A | 13-07-2005 |
| | | CN 1642648 A | 20-07-2005 |
| | | CN 1646221 A | 27-07-2005 |
| | | EP 1478461 A2 | 24-11-2004 |
| | | EP 1478462 A2 | 24-11-2004 |
| | | EP 1478464 A2 | 24-11-2004 |
| | | JP 2005518928 T | 30-06-2005 |
| | | JP 2005518929 T | 30-06-2005 |
| | | JP 2005518930 T | 30-06-2005 |
| | | TW 265824 B | 11-11-2006 |
| | | TW 265825 B | 11-11-2006 |
| | | WO 03074175 A2 | 12-09-2003 |
| | | WO 03074176 A2 | 12-09-2003 |