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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
27 January 2022 (27.01.2022)

WIPO | PCT

(10) International Publication Number
WO 2022/018081 A1

(51) International Patent Classification:
B01J 23/42 (2006.01) *B01J 29/44* (2006.01)
B01J 23/60 (2006.01) *B01J 37/18* (2006.01)
B01J 23/58 (2006.01) *C07C 5/333* (2006.01)

(21) International Application Number:
PCT/EP2021/070267

(22) International Filing Date:
20 July 2021 (20.07.2021)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
20186969.0 21 July 2020 (21.07.2020) EP

(71) Applicant: **BASF SE** [DE/DE]; Carl-Bosch-Strasse 38, 67056 Ludwigshafen am Rhein (DE).

(72) Inventors: **GENTZEN, Manuel Frederik**; Carl-Bosch-Strasse 38, 67056 Ludwigshafen am Rhein (DE). **PATCAS, Florina Corina**; Carl-Bosch-Strasse 38, 67065 Ludwigshafen am Rhein (DE). **HAAS, Andreas**; Carl-Bosch-Strasse 38, 67056 Ludwigshafen am Rhein (DE). **BOTTKE, Nils**; Carl-Bosch-Straße 38, 67056 Ludwigshafen am Rhein (DE).

(74) Agent: **ALTMANN, Andreas**; Altmann Stössel Dick Patentanwälte Partg MbB, Isartorplatz 1, 80331 München (DE).

(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, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, IT, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

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

Declarations under Rule 4.17:
— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*
— *of inventorship (Rule 4.17(iv))*

Published:
— *with international search report (Art. 21(3))*

WO 2022/018081 A1

(54) Title: A ZEOLITE CATALYST AND USE THEREOF FOR THE DEHYDROGENATION OF ALKANES

(57) Abstract: The present invention relates to a zeolite catalyst, wherein the zeolite catalyst comprises a zeolitic material, wherein the framework of the zeolitic material comprises Y02 and X203, wherein Y is a tetravalent element and X is a trivalent element, wherein the Y : X molar ratio of Y and X contained in the framework of the zeolitic material is comprised in the range of from 500 to 10,000, and wherein the zeolite catalyst further comprises Pt which is supported on the zeolitic material. Furthermore, the present invention relates to a molding comprising the zeolite catalyst, as well as to processes for the preparation of the molding. The present invention also relates to a process for the dehydrogenation of alkanes using the inventive zeolite catalyst or molding, as well as to their respective use. In particular, the catalyst can be Pt/ZSM-5, Pt-Zn/ZSM-5, Pt-K/ZSM-5 or Pt-Zn-K / ZSM-5, with the zeolite exhibiting a Si/A I molar ratio of 850.

A Zeolite Catalyst and Use thereof for the Dehydrogenation of Alkanes

TECHNICAL FIELD

The present invention relates to a zeolite catalyst supporting platinum, wherein the zeolite support displays a particular ratio of tetravalent to trivalent elements in its framework structure. Furthermore, the present invention relates to a molding comprising the zeolite catalyst, as well as to processes for the preparation of the molding. The present invention also relates to a process for the dehydrogenation of alkanes using the inventive zeolite catalyst or molding, as well as to their respective use.

INTRODUCTION

Pt based catalysts are known for their ability to catalyze non-oxidative dehydrogenation of alkanes. During these processes a gaseous alkane containing feed stream is contacted with the catalyst at elevated temperatures to give the corresponding alkenes. It is also known that under these comparatively high reaction temperatures, which are necessary in view of thermodynamic constraints, coke formation is one of the root causes for the deactivation of these catalysts. Typically, the coked Pt based catalysts are thus regenerated. However, regeneration of the coked Pt based catalysts usually reduces the productivity of an industrial plant or may require additional resources.

US 5126502 A discloses a dehydrogenation catalyst and to a process for producing the dehydrogenation catalyst. The disclosed catalyst can be a silicalite (Al-free zeolite) impregnated with Pt and Zn. The catalyst was tested as being suitable in iso-butane dehydrogenation. According US 5126502 A, it is preferred that the catalyst is substantially free of alkali metals.

US 7432406 B1 discloses a zeolite L ion exchanged with Pt, Sn, and K. Said material was tested as being suitable for dehydrogenation of isobutene.

US 2019/232255 A1 discloses a catalyst useful for the dehydrogenation of hydrocarbons. The catalyst comprises a platinum-group metal, an assistant metal, and an alkali metal or alkaline earth metal component supported on a carrier. In the examples, a catalyst comprising Pt, Sn, and K supported on alumina was tested for propane dehydrogenation.

CN 108579742 A relates to a dehydrogenation catalyst comprising a zirconia-alumina supporting Zn and Pt. As an auxiliary component potassium is disclosed. The prepared catalysts were tested in propane dehydrogenation.

CN 104289218 A relates to a catalyst for dehydrogenation of isobutane to isobutylene. In particular, a catalyst is disclosed comprising gamma-alumina used as support which was impregnated with Pt, Sn, and K. The catalysts were tested in isobutane dehydrogenation.

CN 105521813 A discloses a catalyst molding comprising a ZSM-5 zeolite having a silicon to aluminum ratio in the range of from 100-150, and an alumina binder. On said molding Sn, Zn and Pt are impregnated and the resulting catalysts were tested in propane dehydrogenation.

CN 105582919 A discloses a catalytic material comprising alumina based supports. The support is modified with a Ce-La-O solid solution, doped with Pt, Sn, an alkali metal, and an additional promotor selected from the group consisting of Fe, Co, Ni, Cu or Zn. The catalytic performance of the prepared catalysts was tested for isobutane dehydrogenation.

WO 2010/076928 A1 discloses a catalyst comprising silica or alumina as support impregnated with platinum, an auxiliary metal, and an alkali or alkaline earth metal.

G. J. Siri et al disclose in Materials Letters 2005, 59, 2319-2324 a dehydrogenation catalyst for converting isobutane. The catalyst comprises Pt and Sn supported on gamma alumina and may be modified with an alkaline metal.

M. Tasbihi et al. discloses in Fuel Processing Technology 2007, 88, 883-889 a Pt-Sn-K-gamma-alumina catalyst prepared via co-impregnation of gamma-alumina with Pt, Sn and K.

J. Camacho-Bunquin et al. disclose in ACS Catal. 2018, 8, 10058-10063 a Pt-Zn catalyst prepared via atomic layer deposition. The catalyst is suitable for the production of butadiene from butane.

B. Mallanna Nagaraja et al. discloses in Catalysis Today 2014, 232, 40-52 a Pt-Sn-K tetha alumina catalyst prepared via impregnation. The catalyst was tested for the dehydrogenation of n-butane.

C. Chen et al. discloses in Catal. Sci. Technol. 2019, 9, 1979 a Pt-Zn H-ZSM-5 catalyst, wherein the zeolite has a Si/Al ratio of 260.

DETAILED DESCRIPTION

It was an object of the present invention to provide a catalytic material particularly showing an improved activity for dehydrogenation of an alkane. Further, it was an object of the present invention to provide a catalytic material showing an improved stability and high selectivity, in particular under reaction conditions comprising a comparatively low hydrogen to alkane molar ratio of the feed.

Thus, it has surprisingly been found that a zeolite catalyst or a molding comprising a zeolitic material supporting Pt, Zn, and K shows an improved activity in the dehydrogenation of an alkane, while particularly showing an improved selectivity and stability. Surprisingly, it has been found that doping a zeolite, with Pt, Zn, and K, the side reactions are suppressed yielding a more selective and more stable catalytic material. Furthermore, the catalytic material of the present invention shows a remarkable stability compared to the prior art. The prepared catalytic material also shows high selectivity and stability in n-butane dehydrogenation.

Therefore, the present invention relates to a zeolite catalyst, wherein the zeolite catalyst comprises a zeolitic material, wherein the framework of the zeolitic material comprises YO_2 and X_2O_3, wherein Y is a tetravalent element and X is a trivalent element, wherein the Y : X molar ratio of Y and X contained in the framework of the zeolitic material is comprised in the range of from 500 to 10,000, and wherein the zeolite catalyst further comprises Pt which is supported on the zeolitic material.

Preferably, the zeolite catalyst contains from 0 to 1 wt.-%, preferably from 0 to 0.1 wt.-%, more preferably from 0 to 0.01 wt.-%, more preferably from 0 to 0.001 wt.-%, of Sn calculated as the element and based on 100 wt.-% of YO_2 in the zeolitic material, wherein the zeolite catalyst more preferably is substantially free of Sn.

Preferably, Y is selected from the group consisting of Si, Sn, Ti, Zr, Ge, and a combination of two or more thereof, preferably from the group consisting of Si, Ti, Zr, and a combination of two or more thereof, more preferably from the group consisting of Si, Sn, and a combination thereof, wherein Y is more preferably Si.

Preferably, X is selected from the group consisting of B, Al, Ga, In, and a combination of two or more thereof, preferably from the group consisting of Al, Ga, and a combination thereof, wherein more preferably X is Al.

Preferably, the zeolitic material has a framework structure containing rings with a maximum ring size of 10 T-atoms, wherein preferably the zeolitic material displays an MFI framework structure type.

Preferably, the zeolitic material comprises one or more zeolites of the MFI-type framework structure, wherein the one or more zeolites are selected from the group consisting of ZSM-5, [Ga-Si-O]-MFI, AMS-1B, AZ-1, Bor-C, Boralite C, Encilite, FZ-1, LZ-105, Monoclinic H-ZSM-5, Mutinaite, NU-4, NU-5, Silicalite, TS-1, TSZ, TSZ-III, TZ-01, USC-4, USI-108, ZBH, ZKQ-1B, ZMQ-TB, and a mixture of two or more thereof, wherein more preferably the zeolitic material comprises ZSM-5, wherein more preferably the zeolitic material consists of ZSM-5.

Preferably, the zeolite catalyst comprises Pt in an amount in the range of from 0.1 to 5 wt.-%, preferably in the range of from 0.2 to 1 wt.-%, more preferably in the range of from 0.3 to 0.8

wt.-%, more preferably in the range of from 0.4 to 0.6 wt.-%, calculated as the element and based on 100 wt.-% of YO_2 in the zeolitic material.

Preferably, the zeolite catalyst comprises Pt in elemental form and/or as counter-ion at an ion exchange site of the framework structure.

Preferably, the zeolite catalyst further comprises Zn, wherein Zn is supported on the zeolitic material. Preferably, the zeolite catalyst comprises Zn in elemental form and/or as counter-ion at an ion exchange site of the framework structure. More preferably, the zeolite catalyst comprises Pt and Zn in elemental form, wherein preferably Pt and Zn form a PtZn alloy.

Preferably, the zeolite catalyst comprises Zn in an amount ranging from 0.1 to 10 wt.-%, preferably in the range of from 0.3 to 5 wt.-%, more preferably in the range of from 0.5 to 4.5 wt.-%, more preferably in the range of from 0.7 to 4.1 wt.-%, more preferably in the range of from 0.8 to 1.5 wt.-%, more preferably in the range of from 0.9 to 1.1 wt.-%, calculated as the element and based on 100 wt.-% of YO_2 in the zeolitic material.

Preferably, the zeolite catalyst further comprises one or more metals selected from the group consisting of alkali metals and alkaline earth metals, wherein the one or more metals are respectively supported on the zeolitic material, wherein the one or more metals are preferably selected from the group consisting of Na, K, and Mg, wherein more preferably the zeolite catalyst further comprises K. More preferably, the zeolite catalyst comprises the one or more metals selected from the group consisting of alkali metals and alkaline earth metals as counter-ion at an ion exchange site of the framework structure.

Preferably, the zeolite catalyst comprises the one or more metals selected from the group consisting of alkali metals and alkaline earth metals in an amount ranging from 0.01 to 8 wt.-% calculated as the element and based on 100 wt.-% of YO_2 in the zeolitic material, wherein preferably the zeolite catalyst comprises the one or more metals selected from the group consisting of alkali metals and alkaline earth metals in an amount ranging from 0.05 to 6 wt.-%, more preferably from 0.1 to 5 wt.-%, more preferably from 0.15 to 4.5 wt.-%, more preferably from 0.2 to 4 wt.-%, more preferably from 0.25 to 3.5 wt.-%, more preferably from 0.5 to 3.25 wt.-%, more preferably from 0.75 to 3 wt.-%, more preferably from 1 to 2.75 wt.-%, more preferably from 1.25 to 2.5 wt.-%, more preferably from 1.5 to 2.25 wt.-%, and more preferably from 1.75 to 2 wt.-%.

Preferably, the Y : X molar ratio of Y and X contained in the framework of the zeolitic material is comprised in the range of from 750 to 6,000, preferably in the range of from 800 to 4,000, more preferably in the range of from 850 to 3,700, more preferably in the range of from 900 to 3,500, more preferably in the range of from 1,000 to 3,300, more preferably in the range of from 1,100 to 3,000, more preferably in the range of from 1,200 to 2,800, more preferably in the range of from 1,300 to 2,500, more preferably in the range of from 1,400 to 2,300, more preferably in the range of from 1,500 to 2,000, and more preferably in the range of from 1,600 to 1,800.

Preferably, the zeolite catalyst contains from 0 to 1 wt.-%, preferably from 0 to 0.1 wt.-%, more preferably from 0 to 0.01 wt.-%, more preferably from 0 to 0.005 wt.-%, more preferably from 0 to 0.003 wt.-%, of Na calculated as the element and based on 100 wt.-% of YO_2 in the zeolitic material, wherein the zeolite catalyst more preferably is substantially free of Na.

The present invention further relates a molding comprising a zeolite catalyst according to any of the particular and preferred embodiments of the zeolite catalyst according to the present application.

Preferably, the molding further comprises a binder, wherein the binder is selected from the group consisting of silica, alumina, titania, zirconia, magnesia, a silica-alumina mixed oxide, a silica-titania mixed oxide, a silica-zirconia mixed oxide, a silica-lanthana mixed oxide, a silica-zirconia-lanthana mixed oxide, an alumina-titania mixed oxide, an alumina-zirconia mixed oxide, an alumina-lanthana mixed oxide, an alumina-zirconia-lanthana mixed oxide, a titania-zirconia mixed oxide, and a mixture and/or mixed oxide of two or more thereof, preferably from the group consisting of silica, alumina, a silica-alumina mixed oxide, and mixture of two or more thereof, wherein more preferably the binder comprises silica, wherein more preferably the binder consists of silica.

Preferably, the molding is in the form of an extrudate, wherein the molding preferably is a strand, preferably having a hexagonal, rectangular, quadratic, triangular, oval, or circular cross-section, more preferably a circular cross-section, wherein the cross-section preferably has a diameter in the range of from 0.5 to 5 mm, preferably in the range of from 1 to 3 mm, more preferably in the range of from 1.5 to 2 mm.

Preferably, from 99 to 100 wt.-%, preferably from 99.5 to 100 wt.-%, more preferably from 99.9 to 100 wt.-%, of the molding consists of the zeolite catalyst and the binder.

Alternatively, the molding preferably does not contain a binder, wherein the molding is then preferably in the form of a tablet.

Preferably, the molding contains from 0 to 1 wt.-%, preferably from 0 to 0.1 wt.-%, more preferably from 0 to 0.01 wt.-%, more preferably from 0 to 0.001 wt.-%, of Sn calculated as the element and based on 100 wt.-% of YO_2 in the zeolitic material, wherein the molding more preferably is substantially free of Sn.

Preferably, the molding contains from 0 to 1 wt.-%, preferably from 0.001 to 0.1 wt.-%, more preferably from 0.01 to 0.05 wt.-%, more preferably from 0.02 to 0.03 wt.-%, of Al calculated as the element and based on 100 wt.-% of YO_2 in the zeolitic material.

Preferably, the molding contains from 0 to 1 wt.-%, preferably from 0 to 0.1 wt.-%, more preferably from 0 to 0.01 wt.-%, more preferably from 0 to 0.005 wt.-%, more preferably from 0 to 0.003 wt.-%, more preferably from 0 to 0.001 wt.-%, more preferably from 0 to 0.0005 wt.-%, more

preferably from 0 to 0.0001 wt.-%, of Na calculated as the element and based on 100 wt.-% of YO_2 in the zeolitic material, wherein the molding more preferably is substantially free of Na.

The present invention further relates a process for the preparation of a molding, preferably of a molding according to any of the particular and preferred embodiments of the molding according to the present application, wherein the process comprises

(a) preparing a mixture comprising a zeolitic material and optionally a source of a binder;
(b) shaping the mixture obtained from (a); to obtain a precursor molding;
(b') optionally drying of the precursor of the molding in a gas atmosphere
(c) calcining the precursor molding in a gas atmosphere;
(d) subjecting the calcined precursor molding obtained from (c) to one or more impregnation procedures, preferably one or more ion exchange procedures, with a source of Pt, optionally with a source of Zn, and optionally with a source of one or more metals selected from the group consisting of alkali metals and alkaline earth metals, to obtain the molding;

wherein the framework of the zeolitic material comprises YO_2 and X_2O_3, wherein Y is a tetravalent element and X is a trivalent element, and wherein the Y : X molar ratio of Y and X contained in the framework of the zeolitic material is comprised in the range of from 500 to 10,000.

Preferably, in (d) the one or more metals selected from the group consisting of alkali metals and alkaline earth metals is selected from the group consisting of Na, K, and Mg, wherein preferably the calcined precursor molding obtained from (c) is subject to one or more impregnation procedures, preferably one or more ion exchange procedures, with a source of K.

Preferably, the Y : X molar ratio of Y and X contained in the framework of the zeolitic material is comprised in the range of from 750 to 6,000, preferably in the range of from 800 to 4,000, more preferably in the range of from 850 to 3,700, more preferably in the range of from 900 to 3,500, more preferably in the range of from 1,000 to 3,300, more preferably in the range of from 1,100 to 3,000, more preferably in the range of from 1,200 to 2,800, more preferably in the range of from 1,300 to 2,500, more preferably in the range of from 1,400 to 2,300, more preferably in the range of from 1,500 to 2,000, and more preferably in the range of from 1,600 to 1,800.

Preferably, (a) comprises

(a.1) preparing a mixture comprising a zeolitic material and a first additive;
(a.2) adding a source of a binder to the mixture obtained from (a.1);
(a.3) optionally adding ammonia and optionally adding a first solvent system to the mixture prepared in (a.1) or to the mixture obtained from (a.2);
(a.4) optionally adding a second additive to the mixture prepared in (a.1), to the mixture obtained from (a.2) or to the mixture obtained from (a.3).

Preferably, Y contained in the framework of the zeolitic material is selected from the group consisting of Si, Sn, Ti, Zr, Ge, and a combination of two or more thereof, preferably from the group consisting of Si, Ti, Zr, and a combination of two or more thereof, more preferably from the group consisting of Si, Sn, and a combination thereof, wherein more preferably Y is Si.

Preferably, X contained in the framework of the zeolitic material is selected from the group consisting of B, Al, Ga, In, and a combination of two or more thereof, preferably from the group consisting of Al, Ga, and a combination thereof, wherein more preferably X is Al.

Preferably, the zeolitic material displays an MFI framework structure type. More preferably, the zeolitic material comprises one or more zeolites of the MFI-type framework structure, wherein the one or more zeolites are selected from the group consisting of ZSM-5, [As-Si-O]-MFI, [Fe-Si-O]-MFI, [Ga-Si-O]-MFI, AMS-1B, AZ-1, Bor-C, Boralite C, Encilite, FZ-1, LZ-105, Monoclinic H-ZSM-5, Mutinaite, NU-4, NU-5, Silicalite, TS-1, TSZ, TSZ-III, TZ-01, USC-4, USI-108, ZBH, ZKQ-1B, ZMQ-TB, and a mixture of two or more thereof, wherein more preferably the zeolitic material comprises ZSM-5, wherein more preferably the zeolitic material consists of ZSM-5.

Preferably, the source of the binder comprises one or more sources of a metal oxide and/or of a metalloid oxide, more preferably one or more sources of a metal oxide and/or of a metalloid oxide selected from the group consisting of silica, alumina, titania, zirconia, lanthana, magnesia, and a mixture and/or a mixed oxide of two or more thereof, more preferably from the group consisting of silica, alumina, titania, zirconia, magnesia, a silica-alumina mixed oxide, a silica-titania mixed oxide, a silica-zirconia mixed oxide, a silica-lanthana mixed oxide, a silica-zirconia-lanthana mixed oxide, an alumina-titania mixed oxide, an alumina-zirconia mixed oxide, an alumina-lanthana mixed oxide, an alumina-zirconia-lanthana mixed oxide, a titania-zirconia mixed oxide, and a mixture and/or a mixed oxide of two or more thereof, more preferably from the group consisting of silica, alumina, a silica-alumina mixed oxide, and a mixture of two or more thereof. Preferably, the one or more sources of a metal oxide and/or of a metalloid oxide are salts, preferably hydroxide and/or acetate salts.

Preferably, the mixture obtained from (a) displays a weight ratio of the zeolitic material to the source of the binder, zeolitic material : source of the binder, in the range of from 0.5:1 to 10:1, preferably in the range of from 2:1 to 6:1, more preferably in the range of from 3.5:1 to 4.5:1, more preferably in the range of from 3.9:1 to 4.1:1.

Preferably, the source of the binder comprises a second solvent system, wherein the second solvent system preferably comprises one or more solvents, wherein preferably the second solvent system comprises one or more hydrophilic solvents, the hydrophilic solvents preferably being selected from the group consisting of polar solvents, more preferably from the group consisting of polar protic solvents, wherein more preferably the second solvent system comprises one or more polar protic solvents selected from the group consisting of water, an alcohol, and a mixture of two or more thereof, more preferably from the group consisting of water, a C1-C5 alcohol, and a mixture of two or more thereof, more preferably from the group consisting of water, a C1-C4 alcohol, and a mixture of two or more thereof, more preferably from the group consisting of water, a C1-C3 alcohol, and a mixture of two or more thereof, more preferably from the group consisting of water, methanol, ethanol, propanol, and a mixture of two or more thereof, more preferably from the group consisting of water, ethanol, and a mixture of two or more thereof, wherein more preferably the second solvent system comprises water and/or ethanol, and

wherein more preferably the second solvent system comprises water, wherein even more preferably the second solvent system consists of water.

Preferably, the source of the binder comprises a second solvent system, wherein the mixture obtained from (a) displays a weight ratio of the second solvent system to the source of the binder, second solvent system : source of the binder, in the range of from 0.5:1 to 5:1, preferably in the range of from 1:1 to 2:1, more preferably in the range of from 1.2:1 to 1.8:1, more preferably in the range of from 1.4:1 to 1.6:1.

Preferably, the mixture prepared in (a) further comprises a first additive, wherein the first additive preferably is a pore forming agent, wherein the first additive more preferably is selected from the group consisting of a polymers, a carbohydrate, graphite, and a mixture of two or more thereof, more preferably from the group consisting of a polymeric vinyl compound, a polyalkylene oxide, a polyacrylate, a polyolefin, a polyamide, a polyester, cellulose, a cellulose derivative, a sugar, and a mixture of two or more thereof, more preferably from the group consisting of polystyrene, a C2-C3 polyalkylene oxide, a cellulose derivative, a sugar, and a mixture of two or more thereof, more preferably from the group consisting of polystyrene, polyethylene oxide, a C1-C2 hydroxyalkylated and/or a C1-C2 alkylated cellulose derivative, a sugar, and a mixture of two or more thereof, more preferably from the group consisting of polystyrene, polyethylene oxide, hydroxyethylcellulose, and a mixture of two or more thereof,
wherein more preferably the first additive consists of one or more of polystyrene, polyethylene oxide, hydroxyethyl cellulose, and a mixture of two or more thereof, and more preferably wherein the first additive consists of a hydroxyethylcellulose.

Preferably, a first solvent system is added according to (a.3), wherein the first solvent system comprises one or more solvents, wherein preferably the first solvent system comprises one or more hydrophilic solvents, the hydrophilic solvents preferably being selected from the group consisting of polar solvents, more preferably from the group consisting of polar protic solvents, wherein more preferably the first solvent system comprises one or more polar protic solvents selected from the group consisting of water, an alcohol, a carboxylic acid, and a mixture of two or more thereof, more preferably from the group consisting of water, a C1-C5 alcohol, a C1-C5 carboxylic acid, and a mixture of two or more thereof, more preferably from the group consisting of water, a C1-C4 alcohol, a C1-C4 carboxylic acid, and a mixture of two or more thereof, more preferably from the group consisting of water, a C1-C3 alcohol, a C1-C3 carboxylic acid, and a mixture of two or more thereof, more preferably from the group consisting of water, methanol, ethanol, propanol, formic acid, acetic acid, and a mixture of two or more thereof, more preferably from the group consisting of water, ethanol, acetic acid, and a mixture of two or more thereof, wherein more preferably the first solvent system comprises water and/or ethanol, and wherein more preferably the first solvent system comprises water, wherein even more preferably the first solvent system consists of water.

Preferably, ammonia is added according to (a.3) and wherein a first solvent system is added according to (a.3), wherein the mixture obtained from (a) displays a weight ratio of the first solvent

system to ammonia, first solvent system : ammonia, in the range of from 0.5:1 to 10:1, preferably in the range of from 2:1 to 5:1, more preferably in the range of from 2.5:1 to 3.5:1, more preferably in the range of from 2.9:1 to 3.1:1.

Preferably, the mixture prepared in (a) further comprises a second additive, wherein the second additive preferably is a pore forming agent, wherein the second additive more preferably is selected from the group consisting of a polymers, a carbohydrate, graphite, and a mixture of two or more thereof, more preferably from the group consisting of a polymeric vinyl compound, a polyalkylene oxide, a polyacrylate, a polyolefin, a polyamide, a polyester, cellulose, a cellulose derivative, a sugar, and a mixture of two or more thereof, more preferably from the group consisting of polystyrene, a C2-C3 polyalkylene oxide, a cellulose derivative, a sugar, and a mixture of two or more thereof, more preferably from the group consisting of polystyrene, polyethylene oxide, a C1-C2 hydroxyalkylated and/or a C1-C2 alkylated cellulose derivative, a sugar, and a mixture of two or more thereof, more preferably from the group consisting of polystyrene, polyethylene oxide, hydroxyethylcellulose, and a mixture of two or more thereof, wherein more preferably the second additive consists of one or more of polystyrene, polyethylene oxide, hydroxyethyl cellulose, and a mixture of two or more thereof, and more preferably wherein the second additive consists of a polyethylene oxide.

Preferably, (b) is performed by extruding the mixture obtained from (a), preferably to a strand, more preferably to a strand having a hexagonal, rectangular, quadratic, triangular, oval, or circular cross-section, preferably a circular cross-section, wherein the cross-section preferably has a diameter in the range of from 0.5 to 5 mm, more preferably in the range of from 1 to 2 mm, more preferably in the range of from 1.2 to 1.8 mm, more preferably in the range of from 1.3 to 1.6 mm.

Preferably, the gas atmosphere in (c) comprises air, wherein preferably the gas atmosphere in (c) consists of air. Preferably, the gas atmosphere in (c) has a temperature in the range of from 400 to 700 °C, preferably in the range of from 500 to 650 °C, more preferably in the range of from 575 to 625 °C.

Preferably, in (d) the source of Pt comprises one or more of an ammine stabilized hydroxo Pt(II) complex, hexachloroplatinic acid, potassium hexachloroplatinate, and ammonium hexachloroplatinate, preferably one or more of tetraammineplatinum chloride, and tetraammineplatinum nitrate, wherein the source of Pt preferably comprises, more preferably consists of, tetraammineplatinum chloride.

Preferably, in (d) the source of Zn comprises one or more of zink chloride, zink fluoride, zink sulfate, zink carbonate, zink nitrate, zink sulfate, zink phosphate, zink stearate, and zink acetate, preferably one or more of zink nitrate, zink chloride, and zink acetate, wherein the source of Zn preferably comprises, more preferably consists of, zink acetate.

Preferably, in (d) the source of K comprises one or more of potassium acetate, potassium bromide, potassium carbonate, potassium chloride, potassium dihydrogenphosphate, potassium diphosphate, potassium disulfate, potassium ethanolate, potassium fluoride, potassium formate, potassium hexachloroplatinate, potassium hydrogen carbonate, potassium hydrogensulfate, potassium iodide, potassium nitrate, potassium methanolate, potassium oxide, potassium oxalate, potassium phosphate, potassium sulfate, and potassium hydroxide, preferably one or more of potassium acetate, potassium nitrate, potassium chloride, and potassium hydroxide, wherein the source of K preferably comprises, more preferably consists of, potassium hydroxide.

Preferably, the process further comprises after (c) and prior to (d)

(c.1) subjecting the calcined precursor molding obtained from (c) to a treatment with H^+ and/or NH_4^+, preferably with H^+;

(c.2) optionally isolating the treated precursor molding obtained from (c.1);

(c.3) optionally washing the treated precursor molding obtained from (c.1) or the isolated precursor molding obtained from (c.2);

(c.3) optionally drying the treated precursor molding obtained from (c.1) or the washed precursor molding obtained from (c.2);

(c.4) calcining the treated precursor molding obtained from (c.1), the washed precursor molding obtained from (c.2), or the dried precursor molding obtained from (c.3);

wherein (c.1) preferably is repeated 1 to 3 times, more preferably once or twice, more preferably once.

Preferably, subjecting the calcined precursor molding obtained from (c) to treatment with H^+ and/or NH_4^+ according to (c.1) is performed in an aqueous medium, preferably in a solvent system comprising water.

Preferably, subjecting the calcined precursor molding to treatment with H^+ and/or $NH_4^+$is performed in an aqueous medium at a pH in the range of from 3 to 8, preferably at a pH in the range of from 4 to 7, more preferably at a pH in the range of from 5 to 6.

Preferably, isolating the treated precursor molding in (c.2) is performed by filtration.

Preferably, washing the ion exchanged precursor molding obtained from (c.1) or the isolated precursor molding obtained from (c.2) in (c.3) is performed with water, preferably deionized water.

Preferably, (d) comprises

(d.1) subjecting the calcined precursor molding obtained from (c) to ion exchange with a source of Zn;

(d.2) optionally drying the ion exchanged molding obtained from (d.1) in a gas atmosphere;

(d.3) calcining the dried molding obtained from (d.1) or (d.2) in a gas atmosphere;

(d.4) subjecting the calcined precursor molding obtained from (d.3) to ion exchange with a source of K and a source of Pt, preferably simultaneously;
(d.5) drying the ion exchanged molding from (d.4) in a gas atmosphere;
(d.6) optionally calcining the dried molding obtained from (d.4) or (d.5) in a gas atmosphere.

Preferably, (d.4) comprises
(d.4.a) subjecting the calcined precursor molding obtained from (d.3) to ion exchange with a source of K;
(d.4.b) optionally drying the ion exchanged molding obtained from (d.4.a) in a gas atmosphere;
(d.4.c) optionally calcining the dried molding obtained from (d.4.a) or (d.4.b) in a gas atmosphere;
(d.4.d) subjecting the calcined precursor molding obtained from (d.4.c) to ion exchange with a source of Pt.

Preferably, the gas atmosphere in one or more of (d.2), (d.3), (d.4.b), (d.4.c), (d.5), and (d.6) comprises air, wherein preferably the gas atmosphere consists of air.

Preferably, the gas atmosphere in one or more of (d.2), (d.4.b), and (d.5) has a temperature in the range of from 60 to 100 °C, preferably in the range of from 70 to 90 °C, more preferably in the range of from 75 to 85 °C.

Preferably, the gas atmosphere in one or more of (d.3), (d.4.c), and (d.6) has a temperature in the range of from 200 to 700 °C, preferably in the range of from 400 to 650 °C, more preferably in the range of from 500 to 600 °C, more preferably in the range of from 525 to 575 °C.

The present invention further relates a molding obtainable and/or obtained according to any of the particular and preferred embodiments of the process of the present invention for the preparation of a molding.

The present invention further relates a process for the dehydrogenation of one or more alkanes comprising
(I) providing a reactor comprising a reaction zone, wherein the reaction zone comprises a zeolite catalyst according to any of the particular and preferred embodiments of the zeolite catalyst according to the present application, or a molding according to any of the particular and preferred embodiments of the molding according to the present application;
(I') optionally subjecting the zeolite catalyst provided in (I) to a reduction treatment
(II) providing a feed comprising one or more alkanes into the reaction zone according to (I) or (I') under reaction conditions in the reaction zone; obtaining a product mixture;
(III) separating the product mixture from the reaction zone.

Preferably, the one or more alkanes are selected from the group consisting of propane, n-butane, isobutane, n-pentane, isopentane, neopentane, 2-methylpentane, 3-methylpentane, 2,3-dimethylpentane, 2,2-dimethylpentane, n-hexane, and a mixture of two or more thereof, wherein the one or more alkanes preferably comprise, more preferably consists of, propane, n-butane, isobutane, and a mixture of two or more thereof.

Preferably, the reduction treatment in (I') comprises treating the zeolite catalyst according to any of the particular and preferred embodiments of the zeolite catalyst according to the present application, or the molding according to any of the particular and preferred embodiments of the molding according to the present application, with a hydrogen containing atmosphere.

Preferably, the hydrogen has a temperature in the range of from 300 to 600 °C, preferably in the range of from 350 to 500 °C, more preferably in the range of from 390 to 410 °C.

Preferably, the process is carried out in batch mode or in continuous mode.

Preferably, the zeolite catalyst according to any of the particular and preferred embodiments of the zeolite catalyst according to the present application, or the molding according to any of the particular and preferred embodiments of the molding according to the present application, is present in a fixed bed or in a fluidized bed.

Preferably, the feed comprises one or more of propane, n-butane, isobutane, n-pentane, isopentane, neopentane, 2-methylpentane, 3-methylpentane, 2,3-dimethylpentane, 2,2-dimethylpentane, and n-hexane, preferably one or more of propane, n-butane, and isobutane.

Preferably, the feed further comprises one or more of hydrogen, and nitrogen, preferably hydrogen and nitrogen.

Preferably, the feed further comprises hydrogen, wherein a molar ratio of the one or more alkanes to hydrogen is in the range of from 1:2 to 1:0.01, preferably in the range of from 1:1.5 to 1:0.5, more preferably in the range of from 1:1.2 to 1:0.8.

Preferably, the feed further comprises nitrogen, wherein a molar ratio of the one or more alkanes to nitrogen is in the range of from 1:1 to 1:0.01, preferably in the range of from 1:0.5 to 1:0.05, more preferably in the range of from 1:0.1 to 1:0.075.

Preferably, the feed comprises from 0 to 1 volume-%, preferably from 0 to 0.1 volume-%, more preferably from 0 to 0.01 volume-%, more preferably from 0 to 0.001 volume-%, water, wherein the feed more preferably is substantially free of water.

Preferably, the reaction conditions in (II) comprise a temperature of from 400 to 700 °C, preferably in the range of from 450 to 650 °C.

Preferably, the reaction conditions in (II) comprise a pressure in the range of from 0 to 5 bar(abs), preferably in the range of from 0.5 to 3 bar(abs), more preferably in the range of from 1 to 2 bar(abs), more preferably in the range of from 1.3 to 1.7 bar(abs), more preferably in the range of from 1.4 to 1.6 bar(abs). The unit bar or bar(abs) refers to an absolute pressure of 10^5 Pa.

Preferably, the providing the feed in (II) is carried out at a gas hourly space velocity (GHSV) in the range of from 300 to 2000 h^{-1}, preferably in the range of from 500 to 1500 h^{-1}, preferably in the range of from 800 to 1200 h^{-1}.

Preferably, further comprising after (III)

(IV) separating the zeolite catalyst or the molding from the reaction zone.

Preferably, further comprising after (IV)

(V) recycling the zeolite catalyst or the molding to (I).

Preferably, after (IV) and prior to (V) the zeolite catalyst or the molding is not subject to a step of washing or drying, wherein preferably the zeolite catalyst or the molding is not subject to any treatment after (IV) and prior to (V).

Preferably, the zeolite catalyst or the molding is recycled n times, wherein n is a natural number equal or higher than 1, wherein n preferably ranges from 1 to 100, more preferably from 1 to 75, more preferably from 1 to 50, more preferably from 1 to 20, more preferably from 1 to 10, and more preferably from 1 to 5.

The present invention further relates a use of a zeolite catalyst according to any of the particular and preferred embodiments of the zeolite catalyst according to the present application, or of a molding according to any of the particular and preferred embodiments of the molding according to the present application, as a dehydrogenation catalyst, preferably for the dehydrogenation of one or more alkanes, more preferably for the dehydrogenation of one or more alkanes selected from the group consisting of propane, n-butane, isobutane, n-pentane, isopentane, neopentane, 2-methylpentane, 3-methylpentane, 2,3-dimethylpentane, 2,2-dimethylpentane, n-hexane, and a mixture of two or more thereof, and more preferably for the dehydrogenation of one or more alkanes selected from the group consisting of propane, n-butane, isobutane, and a mixture of two or more thereof.

The present invention is further illustrated by the following set of embodiments and combinations of embodiments resulting from the dependencies and back-references as indicated. In particular, it is noted that in each instance where a range of embodiments is mentioned, for example in the context of a term such as "The zeolite catalyst of any one of embodiments 1 to 4", every embodiment in this range is meant to be explicitly disclosed for the skilled person, i.e. the wording of this term is to be understood by the skilled person as being synonymous to "The ze-

olite catalyst of any one of embodiments 1, 2, 3, and 4". Further, it is explicitly noted that the following set of embodiments is not the set of claims determining the extent of protection, but represents a suitably structured part of the description directed to general and preferred aspects of the present invention.

According to an embodiment (1), the present invention relates a zeolite catalyst, wherein the zeolite catalyst comprises a zeolitic material, wherein the framework of the zeolitic material comprises YO_2 and X_2O_3, wherein Y is a tetravalent element and X is a trivalent element, wherein the Y : X molar ratio of Y and X contained in the framework of the zeolitic material is comprised in the range of from 500 to 10,000, and wherein the zeolite catalyst further comprises Pt which is supported on the zeolitic material.

A preferred embodiment (2) concretizing embodiment (1), wherein the zeolite catalyst contains from 0 to 1 wt.-%, preferably from 0 to 0.1 wt.-%, more preferably from 0 to 0.01 wt.-%, more preferably from 0 to 0.001 wt.-%, of Sn calculated as the element and based on 100 wt.-% of YO_2 in the zeolitic material, wherein the zeolite catalyst more preferably is substantially free of Sn.

A preferred embodiment (3) concretizing embodiment (1) or (2), wherein Y is selected from the group consisting of Si, Sn, Ti, Zr, Ge, and a combination of two or more thereof, preferably from the group consisting of Si, Ti, Zr, and a combination of two or more thereof, more preferably from the group consisting of Si, Sn, and a combination thereof, wherein Y is more preferably Si.

A preferred embodiment (4) concretizing any one of embodiments (1) to (3), wherein X is selected from the group consisting of B, Al, Ga, In, and a combination of two or more thereof, preferably from the group consisting of Al, Ga, and a combination thereof, wherein more preferably X is Al.

A preferred embodiment (5) concretizing any one of embodiments (1) to (4), wherein the zeolitic material has a framework structure containing rings with a maximum ring size of 10 T-atoms, wherein preferably the zeolitic material displays an MFI framework structure type.

A preferred embodiment (6) concretizing any one of embodiments (1) to (5), wherein the zeolitic material comprises one or more zeolites of the MFI-type framework structure, wherein the one or more zeolites are selected from the group consisting of ZSM-5, [Ga-Si-O]-MFI, AMS-1B, AZ-1, Bor-C, Boralite C, Encilite, FZ-1, LZ-105, Monoclinic H-ZSM-5, Mutinaite, NU-4, NU-5, Silicalite, TS-1, TSZ, TSZ-III, TZ-01, USC-4, USI-108, ZBH, ZKQ-1B, ZMQ-TB, and a mixture of two or more thereof, wherein more preferably the zeolitic material comprises ZSM-5, wherein more preferably the zeolitic material consists of ZSM-5.

A preferred embodiment (7) concretizing any one of embodiments (1) to (6), wherein the zeolite catalyst comprises Pt in an amount in the range of from 0.1 to 5 wt.-%, preferably in the range of from 0.2 to 1 wt.-%, more preferably in the range of from 0.3 to 0.8 wt.-%, more preferably in

the range of from 0.4 to 0.6 wt.-%, calculated as the element and based on 100 wt.-% of YO_2 in the zeolitic material.

A preferred embodiment (8) concretizing any one of embodiments (1) to (7), wherein the zeolite catalyst comprises Pt in elemental form and/or as counter-ion at an ion exchange site of the framework structure.

A preferred embodiment (9) concretizing any one of embodiments (1) to (8), wherein the zeolite catalyst further comprises Zn, wherein Zn is supported on the zeolitic material.

A preferred embodiment (10) concretizing embodiment (9), wherein the zeolite catalyst comprises Zn in elemental form and/or as counter-ion at an ion exchange site of the framework structure.

A preferred embodiment (11) concretizing embodiment (9) or (10), wherein the zeolite catalyst comprises Pt and Zn in elemental form, wherein preferably Pt and Zn form a PtZn alloy.

A preferred embodiment (12) concretizing any one of embodiments (9) to (11), wherein the zeolite catalyst comprises Zn in an amount ranging from 0.1 to 10 wt.-%, preferably in the range of from 0.3 to 5 wt.-%, more preferably in the range of from 0.5 to 4.5 wt.-%, more preferably in the range of from 0.7 to 4.1 wt.-%, more preferably in the range of from 0.8 to 1.5 wt.-%, more preferably in the range of from 0.9 to 1.1 wt.-%, calculated as the element and based on 100 wt.-% of YO_2 in the zeolitic material.

A preferred embodiment (13) concretizing any one of embodiments (1) to (12), wherein the zeolite catalyst further comprises one or more metals selected from the group consisting of alkali metals and alkaline earth metals, wherein the one or more metals are respectively supported on the zeolitic material, wherein the one or more metals are preferably selected from the group consisting of Na, K, and Mg, wherein more preferably the zeolite catalyst further comprises K.

A preferred embodiment (14) concretizing embodiment (13), wherein the zeolite catalyst comprises the one or more metals selected from the group consisting of alkali metals and alkaline earth metals as counter-ion at an ion exchange site of the framework structure.

A preferred embodiment (15) concretizing embodiment (13) or (14), wherein the zeolite catalyst comprises the one or more metals selected from the group consisting of alkali metals and alkaline earth metals in an amount ranging from 0.01 to 8 wt.-% calculated as the element and based on 100 wt.-% of YO_2 in the zeolitic material, wherein preferably the zeolite catalyst comprises the one or more metals selected from the group consisting of alkali metals and alkaline earth metals in an amount ranging from 0.05 to 6 wt.-%, more preferably from 0.1 to 5 wt.-%, more preferably from 0.15 to 4.5 wt.-%, more preferably from 0.2 to 4 wt.-%, more preferably from 0.25 to 3.5 wt.-%, more preferably from 0.5 to 3.25 wt.-%, more preferably from 0.75 to 3

wt.-%, more preferably from 1 to 2.75 wt.-%, more preferably from 1.25 to 2.5 wt.-%, more preferably from 1.5 to 2.25 wt.-%, and more preferably from 1.75 to 2 wt.-%.

A preferred embodiment (16) concretizing any one of embodiments (1) to (15), wherein the Y : X molar ratio of Y and X contained in the framework of the zeolitic material is comprised in the range of from 750 to 6,000, preferably in the range of from 800 to 4,000, more preferably in the range of from 850 to 3,700, more preferably in the range of from 900 to 3,500, more preferably in the range of from 1,000 to 3,300, more preferably in the range of from 1,100 to 3,000, more preferably in the range of from 1,200 to 2,800, more preferably in the range of from 1,300 to 2,500, more preferably in the range of from 1,400 to 2,300, more preferably in the range of from 1,500 to 2,000, and more preferably in the range of from 1,600 to 1,800.

A preferred embodiment (17) concretizing any one of embodiments (1) to (16), wherein the zeolite catalyst contains from 0 to 1 wt.-%, preferably from 0 to 0.1 wt.-%, more preferably from 0 to 0.01 wt.-%, more preferably from 0 to 0.005 wt.-%, more preferably from 0 to 0.003 wt.-%, of Na calculated as the element and based on 100 wt.-% of YO_2 in the zeolitic material, wherein the zeolite catalyst more preferably is substantially free of Na.

According to an embodiment (18), the present invention further relates a molding comprising a zeolite catalyst according to any one of embodiments (1) to (17).

A preferred embodiment (19) concretizing embodiment (18), wherein the molding further comprises a binder, wherein the binder is selected from the group consisting of silica, alumina, titania, zirconia, magnesia, a silica-alumina mixed oxide, a silica-titania mixed oxide, a silica-zirconia mixed oxide, a silica-lanthana mixed oxide, a silica-zirconia-lanthana mixed oxide, an alumina-titania mixed oxide, an alumina-zirconia mixed oxide, an alumina-lanthana mixed oxide, an alumina-zirconia-lanthana mixed oxide, a titania-zirconia mixed oxide, and a mixture and/or mixed oxide of two or more thereof, preferably from the group consisting of silica, alumina, a silica-alumina mixed oxide, and mixture of two or more thereof, wherein more preferably the binder comprises silica, wherein more preferably the binder consists of silica.

A preferred embodiment (20) concretizing embodiment (18) or (19), wherein the molding is in the form of an extrudate, wherein the molding preferably is a strand, preferably having a hexagonal, rectangular, quadratic, triangular, oval, or circular cross-section, more preferably a circular cross-section, wherein the cross-section preferably has a diameter in the range of from 0.5 to 5 mm, preferably in the range of from 1 to 3 mm, more preferably in the range of from 1.5 to 2 mm.

A preferred embodiment (21) concretizing any one of embodiments (18) to (20), wherein from 99 to 100 wt.-%, preferably from 99.5 to 100 wt.-%, more preferably from 99.9 to 100 wt.-%, of the molding consists of the zeolite catalyst and the binder.

A preferred embodiment (22) concretizing embodiment (18), wherein the molding does not contain a binder, wherein the molding is preferably in the form of a tablet.

A preferred embodiment (23) concretizing any one of embodiments (18) to (22), wherein the molding contains from 0 to 1 wt.-%, preferably from 0 to 0.1 wt.-%, more preferably from 0 to 0.01 wt.-%, more preferably from 0 to 0.001 wt.-%, of Sn calculated as the element and based on 100 wt.-% of YO_2 in the zeolitic material, wherein the molding more preferably is substantially free of Sn.

A preferred embodiment (24) concretizing any one of embodiments (18) to (23), wherein the molding contains from 0 to 1 wt.-%, preferably from 0.001 to 0.1 wt.-%, more preferably from 0.01 to 0.05 wt.-%, more preferably from 0.02 to 0.03 wt.-%, of Al calculated as the element and based on 100 wt.-% of YO_2 in the zeolitic material.

A preferred embodiment (25) concretizing any one of embodiments (18) to (24), wherein the molding contains from 0 to 1 wt.-%, preferably from 0 to 0.1 wt.-%, more preferably from 0 to 0.01 wt.-%, more preferably from 0 to 0.005 wt.-%, more preferably from 0 to 0.003 wt.-%, more preferably from 0 to 0.001 wt.-%, more preferably from 0 to 0.0005 wt.-%, more preferably from 0 to 0.0001 wt.-%, of Na calculated as the element and based on 100 wt.-% of YO_2 in the zeolitic material, wherein the molding more preferably is substantially free of Na.

According to an embodiment (26), the present invention further relates a process for the preparation of a molding, preferably of a molding according to any one of embodiments (18) to (25), wherein the process comprises

(a) preparing a mixture comprising a zeolitic material and optionally a source of a binder;
(b) shaping the mixture obtained from (a); to obtain a precursor molding;
(b') optionally drying of the precursor of the molding in a gas atmosphere
(c) calcining the precursor molding in a gas atmosphere;
(d) subjecting the calcined precursor molding obtained from (c) to one or more impregnation procedures, preferably one or more ion exchange procedures, with a source of Pt, optionally with a source of Zn, and optionally with a source of one or more metals selected from the group consisting of alkali metals and alkaline earth metals, to obtain the molding;

wherein the framework of the zeolitic material comprises YO_2 and X_2O_3, wherein Y is a tetravalent element and X is a trivalent element, and wherein the Y : X molar ratio of Y and X contained in the framework of the zeolitic material is comprised in the range of from 500 to 10,000.

A preferred embodiment (27) concretizing embodiment (26), wherein in (d) the one or more metals selected from the group consisting of alkali metals and alkaline earth metals is selected from the group consisting of Na, K, and Mg, wherein preferably the calcined precursor molding obtained from (c) is subject to one or more impregnation procedures, preferably one or more ion exchange procedures, with a source of K.

A preferred embodiment (28) concretizing embodiment (26) or (27), wherein the Y : X molar ratio of Y and X contained in the framework of the zeolitic material is comprised in the range of from 750 to 6,000, preferably in the range of from 800 to 4,000, more preferably in the range of from 850 to 3,700, more preferably in the range of from 900 to 3,500, more preferably in the range of from 1,000 to 3,300, more preferably in the range of from 1,100 to 3,000, more preferably in the range of from 1,200 to 2,800, more preferably in the range of from 1,300 to 2,500, more preferably in the range of from 1,400 to 2,300, more preferably in the range of from 1,500 to 2,000, and more preferably in the range of from 1,600 to 1,800.

A preferred embodiment (29) concretizing any one of embodiments (26) to (28), wherein (a) comprises

(a.1) preparing a mixture comprising a zeolitic material and a first additive;
(a.2) adding a source of a binder to the mixture obtained from (a.1);
(a.3) optionally adding ammonia and optionally adding a first solvent system to the mixture prepared in (a.1) or to the mixture obtained from (a.2);
(a.4) optionally adding a second additive to the mixture prepared in (a.1), to the mixture obtained from (a.2) or to the mixture obtained from (a.3).

A preferred embodiment (30) concretizing any one of embodiments (26) to (29), wherein Y contained in the framework of the zeolitic material is selected from the group consisting of Si, Sn, Ti, Zr, Ge, and a combination of two or more thereof, preferably from the group consisting of Si, Ti, Zr, and a combination of two or more thereof, more preferably from the group consisting of Si, Sn, and a combination thereof, wherein more preferably Y is Si.

A preferred embodiment (31) concretizing any one of embodiments (26) to (30), wherein X contained in the framework of the zeolitic material is selected from the group consisting of B, Al, Ga, In, and a combination of two or more thereof, preferably from the group consisting of Al, Ga, and a combination thereof, wherein more preferably X is Al.

A preferred embodiment (32) concretizing any one of embodiments (26) to (31), wherein the zeolitic material displays an MFI framework structure type.

A preferred embodiment (33) concretizing any one of embodiments (26) to (32), wherein the zeolitic material comprises one or more zeolites of the MFI-type framework structure, wherein the one or more zeolites are selected from the group consisting of ZSM-5, [As-Si-O]-MFI, [Fe-Si-O]-MFI, [Ga-Si-O]-MFI, AMS-1B, AZ-1, Bor-C, Boralite C, Encilite, FZ-1, LZ-105, Monoclinic H-ZSM-5, Mutinaite, NU-4, NU-5, Silicalite, TS-1, TSZ, TSZ-III, TZ-01, USC-4, USI-108, ZBH, ZKQ-1B, ZMQ-TB, and a mixture of two or more thereof, wherein more preferably the zeolitic material comprises ZSM-5, wherein more preferably the zeolitic material consists of ZSM-5.

A preferred embodiment (34) concretizing any one of embodiments (26) to (33), wherein the source of the binder comprises one or more sources of a metal oxide and/or of a metalloid oxide, more preferably one or more sources of a metal oxide and/or of a metalloid oxide selected

from the group consisting of silica, alumina, titania, zirconia, lanthana, magnesia, and a mixture and/or a mixed oxide of two or more thereof, more preferably from the group consisting of silica, alumina, titania, zirconia, magnesia, a silica-alumina mixed oxide, a silica-titania mixed oxide, a silica-zirconia mixed oxide, a silica-lanthana mixed oxide, a silica-zirconia-lanthana mixed oxide, an alumina-titania mixed oxide, an alumina-zirconia mixed oxide, an alumina-lanthana mixed oxide, an alumina-zirconia-lanthana mixed oxide, a titania-zirconia mixed oxide, and a mixture and/or a mixed oxide of two or more thereof, more preferably from the group consisting of silica, alumina, a silica-alumina mixed oxide, and a mixture of two or more thereof.

A preferred embodiment (35) concretizing embodiment (34), wherein the one or more sources of a metal oxide and/or of a metalloid oxide are salts, preferably hydroxide and/or acetate salts.

A preferred embodiment (36) concretizing any one of embodiments (26) to (35), wherein the mixture obtained from (a) displays a weight ratio of the zeolitic material to the source of the binder, zeolitic material : source of the binder, in the range of from 0.5:1 to 10:1, preferably in the range of from 2:1 to 6:1, more preferably in the range of from 3.5:1 to 4.5:1, more preferably in the range of from 3.9:1 to 4.1:1.

A preferred embodiment (37) concretizing any one of embodiments (26) to (36), wherein the source of the binder comprises a second solvent system, wherein the second solvent system preferably comprises one or more solvents, wherein preferably the second solvent system comprises one or more hydrophilic solvents, the hydrophilic solvents preferably being selected from the group consisting of polar solvents, more preferably from the group consisting of polar protic solvents, wherein more preferably the second solvent system comprises one or more polar protic solvents selected from the group consisting of water, an alcohol, and a mixture of two or more thereof, more preferably from the group consisting of water, a C1-C5 alcohol, and a mixture of two or more thereof, more preferably from the group consisting of water, a C1-C4 alcohol, and a mixture of two or more thereof, more preferably from the group consisting of water, a C1-C3 alcohol, and a mixture of two or more thereof, more preferably from the group consisting of water, methanol, ethanol, propanol, and a mixture of two or more thereof, more preferably from the group consisting of water, ethanol, and a mixture of two or more thereof, wherein more preferably the second solvent system comprises water and/or ethanol, and wherein more preferably the second solvent system comprises water, wherein even more preferably the second solvent system consists of water.

A preferred embodiment (38) concretizing any one of embodiments (26) to (37), wherein the source of the binder comprises a second solvent system, wherein the mixture obtained from (a) displays a weight ratio of the second solvent system to the source of the binder, second solvent system : source of the binder, in the range of from 0.5:1 to 5:1, preferably in the range of from 1:1 to 2:1, more preferably in the range of from 1.2:1 to 1.8:1, more preferably in the range of from 1.4:1 to 1.6:1.

A preferred embodiment (39) concretizing any one of embodiments (26) to (38), wherein the mixture prepared in (a) further comprises a first additive, wherein the first additive preferably is a pore forming agent, wherein the first additive more preferably is selected from the group consisting of a polymers, a carbohydrate, graphite, and a mixture of two or more thereof, more preferably from the group consisting of a polymeric vinyl compound, a polyalkylene oxide, a polyacrylate, a polyolefin, a polyamide, a polyester, cellulose, a cellulose derivative, a sugar, and a mixture of two or more thereof, more preferably from the group consisting of polystyrene, a C2-C3 polyalkylene oxide, a cellulose derivative, a sugar, and a mixture of two or more thereof, more preferably from the group consisting of polystyrene, polyethylene oxide, a C1-C2 hydroxyalkylated and/or a C1-C2 alkylated cellulose derivative, a sugar, and a mixture of two or more thereof, more preferably from the group consisting of polystyrene, polyethylene oxide, hydroxyethylcellulose, and a mixture of two or more thereof,
wherein more preferably the first additive consists of one or more of polystyrene, polyethylene oxide, hydroxyethyl cellulose, and a mixture of two or more thereof, and more preferably wherein the first additive consists of a hydroxyethylcellulose.

A preferred embodiment (40) concretizing any one of embodiments (26) to (39), wherein a first solvent system is added according to (a.3), wherein the first solvent system comprises one or more solvents, wherein preferably the first solvent system comprises one or more hydrophilic solvents, the hydrophilic solvents preferably being selected from the group consisting of polar solvents, more preferably from the group consisting of polar protic solvents, wherein more preferably the first solvent system comprises one or more polar protic solvents selected from the group consisting of water, an alcohol, a carboxylic acid, and a mixture of two or more thereof, more preferably from the group consisting of water, a C1-C5 alcohol, a C1-C5 carboxylic acid, and a mixture of two or more thereof, more preferably from the group consisting of water, a C1-C4 alcohol, a C1-C4 carboxylic acid, and a mixture of two or more thereof, more preferably from the group consisting of water, a C1-C3 alcohol, a C1-C3 carboxylic acid, and a mixture of two or more thereof, more preferably from the group consisting of water, methanol, ethanol, propanol, formic acid, acetic acid, and a mixture of two or more thereof, more preferably from the group consisting of water, ethanol, acetic acid, and a mixture of two or more thereof, wherein more preferably the first solvent system comprises water and/or ethanol, and wherein more preferably the first solvent system comprises water, wherein even more preferably the first solvent system consists of water.

A preferred embodiment (41) concretizing any one of embodiments (29) to (40), wherein ammonia is added according to (a.3) and wherein a first solvent system is added according to (a.3), wherein the mixture obtained from (a) displays a weight ratio of the first solvent system to ammonia, first solvent system : ammonia, in the range of from 0.5:1 to 10:1, preferably in the range of from 2:1 to 5:1, more preferably in the range of from 2.5:1 to 3.5:1, more preferably in the range of from 2.9:1 to 3.1:1.

A preferred embodiment (42) concretizing any one of embodiments (26) to (41), wherein the mixture prepared in (a) further comprises a second additive, wherein the second additive preferably is a pore forming agent, wherein the second additive more preferably is selected from the group consisting of a polymers, a carbohydrate, graphite, and a mixture of two or more thereof, more preferably from the group consisting of a polymeric vinyl compound, a polyalkylene oxide, a polyacrylate, a polyolefin, a polyamide, a polyester, cellulose, a cellulose derivative, a sugar, and a mixture of two or more thereof, more preferably from the group consisting of polystyrene, a C2-C3 polyalkylene oxide, a cellulose derivative, a sugar, and a mixture of two or more thereof, more preferably from the group consisting of polystyrene, polyethylene oxide, a C1-C2 hydroxyalkylated and/or a C1-C2 alkylated cellulose derivative, a sugar, and a mixture of two or more thereof, more preferably from the group consisting of polystyrene, polyethylene oxide, hydroxyethylcellulose, and a mixture of two or more thereof, wherein more preferably the second additive consists of one or more of polystyrene, polyethylene oxide, hydroxyethyl cellulose, and a mixture of two or more thereof, and more preferably wherein the second additive consists of a polyethylene oxide.

A preferred embodiment (43) concretizing any one of embodiments (26) to (42), wherein (b) is performed by extruding the mixture obtained from (a), preferably to a strand, more preferably to a strand having a hexagonal, rectangular, quadratic, triangular, oval, or circular cross-section, preferably a circular cross-section, wherein the cross-section preferably has a diameter in the range of from 0.5 to 5 mm, more preferably in the range of from 1 to 2 mm, more preferably in the range of from 1.2 to 1.8 mm, more preferably in the range of from 1.3 to 1.6 mm.

A preferred embodiment (44) concretizing any one of embodiments (26) to (43), wherein the gas atmosphere in (c) comprises air, wherein preferably the gas atmosphere in (c) consists of air.

A preferred embodiment (45) concretizing any one of embodiments (26) to (44), wherein the gas atmosphere in (c) has a temperature in the range of from 400 to 700 °C, preferably in the range of from 500 to 650 °C, more preferably in the range of from 575 to 625 °C.

A preferred embodiment (46) concretizing any one of embodiments (26) to (45), wherein in (d) the source of Pt comprises one or more of an ammine stabilized hydroxo Pt(II) complex, hexachloroplatinic acid, potassium hexachloroplatinate, and ammonium hexachloroplatinate, preferably one or more of tetraammineplatinum chloride, and tetraammineplatinum nitrate, wherein the source of Pt preferably comprises, more preferably consists of, tetraammineplatinum chloride.

A preferred embodiment (47) concretizing any one of embodiments (26) to (46), wherein in (d) the source of Zn comprises one or more of zink chloride, zink fluoride, zink sulfate, zink carbonate, zink nitrate, zink sulfate, zink phosphate, zink stearate, and zink acetate, preferably one or more of zink nitrate, zink chloride, and zink acetate, wherein the source of Zn preferably comprises, more preferably consists of, zink acetate.

A preferred embodiment (48) concretizing any one of embodiments (26) to (47), wherein in (d) the source of K comprises one or more of potassium acetate, potassium bromide, potassium carbonate, potassium chloride, potassium dihydrogenphosphate, potassium diphosphate, potassium disulfate, potassium ethanolate, potassium fluoride, potassium formate, potassium hexachloroplatinate, potassium hydrogen carbonate, potassium hydrogensulfate, potassium iodide, potassium nitrate, potassium methanolate, potassium oxide, potassium oxalate, potassium phosphate, potassium sulfate, and potassium hydroxide, preferably one or more of potassium acetate, potassium nitrate, potassium chloride, and potassium hydroxide, wherein the source of K preferably comprises, more preferably consists of, potassium hydroxide.

A preferred embodiment (49) concretizing any one of embodiments (26) to (48), wherein the process further comprises after (c) and prior to (d)

(c.1) subjecting the calcined precursor molding obtained from (c) to a treatment with H^+ and/or NH_4^+, preferably with H^+;

(c.2) optionally isolating the treated precursor molding obtained from (c.1);

(c.3) optionally washing the treated precursor molding obtained from (c.1) or the isolated precursor molding obtained from (c.2);

(c.3) optionally drying the treated precursor molding obtained from (c.1) or the washed precursor molding obtained from (c.2);

(c.4) calcining the treated precursor molding obtained from (c.1), the washed precursor molding obtained from (c.2), or the dried precursor molding obtained from (c.3);

wherein (c.1) preferably is repeated 1 to 3 times, more preferably once or twice, more preferably once.

A preferred embodiment (50) concretizing embodiment (49), wherein subjecting the calcined precursor molding obtained from (c) to treatment with H^+ and/or NH_4^+ according to (c.1) is performed in an aqueous medium, preferably in a solvent system comprising water.

A preferred embodiment (51) concretizing embodiment (50), wherein subjecting the calcined precursor molding to treatment with H^+ and/or $NH_4^+$is performed in an aqueous medium at a pH in the range of from 3 to 8, preferably at a pH in the range of from 4 to 7, more preferably at a pH in the range of from 5 to 6.

A preferred embodiment (52) concretizing any one of embodiments (49) to (51), wherein isolating the treated precursor molding in (c.2) is performed by filtration.

A preferred embodiment (53) concretizing any one of embodiments (49) to (52), wherein washing the ion exchanged precursor molding obtained from (c.1) or the isolated precursor molding obtained from (c.2) in (c.3) is performed with water, preferably deionized water.

A preferred embodiment (54) concretizing any one of embodiments (26) to (53), wherein (d) comprises

(d.1) subjecting the calcined precursor molding obtained from (c) to ion exchange with a source of Zn;
(d.2) optionally drying the ion exchanged molding obtained from (d.1) in a gas atmosphere;
(d.3) calcining the dried molding obtained from (d.1) or (d.2) in a gas atmosphere;
(d.4) subjecting the calcined precursor molding obtained from (d.3) to ion exchange with a source of K and a source of Pt, preferably simultaneously;
(d.5) drying the ion exchanged molding from (d.4) in a gas atmosphere;
(d.6) optionally calcining the dried molding obtained from (d.4) or (d.5) in a gas atmosphere.

A preferred embodiment (55) concretizing embodiment (54), wherein (d.4) comprises
(d.4.a) subjecting the calcined precursor molding obtained from (d.3) to ion exchange with a source of K;
(d.4.b) optionally drying the ion exchanged molding obtained from (d.4.a) in a gas atmosphere;
(d.4.c) optionally calcining the dried molding obtained from (d.4.a) or (d.4.b) in a gas atmosphere;
(d.4.d) subjecting the calcined precursor molding obtained from (d.4.c) to ion exchange with a source of Pt.

A preferred embodiment (56) concretizing embodiment (54) or (55), wherein the gas atmosphere in one or more of (d.2), (d.3), (d.4.b), (d.4.c), (d.5), and (d.6) comprises air, wherein preferably the gas atmosphere consists of air.

A preferred embodiment (57) concretizing any one of embodiments (54) to (56), wherein the gas atmosphere in one or more of (d.2), (d.4.b), and (d.5) has a temperature in the range of from 60 to 100 °C, preferably in the range of from 70 to 90 °C, more preferably in the range of from 75 to 85 °C.

A preferred embodiment (58) concretizing embodiment (54) or (57), wherein the gas atmosphere in one or more of (d.3), (d.4.c), and (d.6) has a temperature in the range of from 200 to 700 °C, preferably in the range of from 400 to 650 °C, more preferably in the range of from 500 to 600 °C, more preferably in the range of from 525 to 575 °C.

According to an embodiment (59), the present invention further relates a molding obtainable and/or obtained according to the process of any one of embodiments (26) to (58).

According to an embodiment (60), the present invention further relates a process for the dehydrogenation of one or more alkanes comprising
(I) providing a reactor comprising a reaction zone, wherein the reaction zone comprises a zeolite catalyst according to any one of embodiments (1) to (17), or a molding according to any one of embodiments (18) to (25), and (59);

(I') optionally subjecting the zeolite catalyst provided in (I) to a reduction treatment
(II) providing a feed comprising one or more alkanes into the reaction zone according to (I) or (I') under reaction conditions in the reaction zone; obtaining a product mixture;
(III) separating the product mixture from the reaction zone.

A preferred embodiment (61) concretizing embodiment (60), wherein the one or more alkanes are selected from the group consisting of propane, n-butane, isobutane, n-pentane, isopentane, neopentane, 2-methylpentane, 3-methylpentane, 2,3-dimethylpentane, 2,2-dimethylpentane, n-hexane, and a mixture of two or more thereof, wherein the one or more alkanes preferably comprise, more preferably consists of, propane, n-butane, isobutane, and a mixture of two or more thereof.

A preferred embodiment (62) concretizing embodiment (60) or (61), wherein the reduction treatment in (I') comprises treating the zeolite catalyst according to any one of embodiments (1) to (17), or the molding of any one of embodiments (18) to (25) and (60) with a hydrogen containing atmosphere.

A preferred embodiment (63) concretizing embodiment (62), wherein the hydrogen has a temperature in the range of from 300 to 600 °C, preferably in the range of from 350 to 500 °C, more preferably in the range of from 390 to 410 °C.

A preferred embodiment (64) concretizing any one of embodiments (60) to (63), wherein the process is carried out in batch mode or in continuous mode.

A preferred embodiment (65) concretizing any one of embodiments (60) to (64), wherein the zeolite catalyst according to any one of embodiments (1) to (17), or the molding of any one of embodiments (18) to (25), and 60 is present in a fixed bed or in a fluidized bed.

A preferred embodiment (66) concretizing any one of embodiments (60) to (65), wherein the feed comprises one or more of propane, n-butane, isobutane, n-pentane, isopentane, neopentane, 2-methylpentane, 3-methylpentane, 2,3-dimethylpentane, 2,2-dimethylpentane, and n-hexane, preferably one or more of propane, n-butane, and isobutane.

A preferred embodiment (67) concretizing embodiment (66), wherein the feed further comprises one or more of hydrogen, and nitrogen, preferably hydrogen and nitrogen.

A preferred embodiment (68) concretizing embodiment (66) or (67), wherein the feed further comprises hydrogen, wherein a molar ratio of the one or more alkanes to hydrogen is in the range of from 1:2 to 1:0.01, preferably in the range of from 1:1.5 to 1:0.5, more preferably in the range of from 1:1.2 to 1:0.8.

A preferred embodiment (69) concretizing any one of embodiments (66) to (68), wherein the feed further comprises nitrogen, wherein a molar ratio of the one or more alkanes to nitrogen is

in the range of from 1:1 to 1:0.01, preferably in the range of from 1:0.5 to 1:0.05, more preferably in the range of from 1:0.1 to 1:0.075.

A preferred embodiment (70) concretizing any one of embodiments (60) to (69), wherein the feed comprises from 0 to 1 volume-%, preferably from 0 to 0.1 volume-%, more preferably from 0 to 0.01 volume-%, more preferably from 0 to 0.001 volume-%, water, wherein the feed more preferably is substantially free of water.

A preferred embodiment (71) concretizing any one of embodiments (60) to (70), wherein the reaction conditions in (II) comprise a temperature of from 400 to 700 °C, preferably in the range of from 450 to 650 °C.

A preferred embodiment (72) concretizing any one of embodiments (60) to (71), wherein the reaction conditions in (II) comprise a pressure in the range of from 0 to 5 bar(abs), preferably in the range of from 0.5 to 3 bar(abs), more preferably in the range of from 1 to 2 bar(abs), more preferably in the range of from 1.3 to 1.7 bar(abs), more preferably in the range of from 1.4 to 1.6 bar(abs).

A preferred embodiment (73) concretizing any one of embodiments (60) to (72), wherein the providing the feed in (II) is carried out at a gas hourly space velocity (GHSV) in the range of from 300 to 2000 h^{-1}, preferably in the range of from 500 to 1500 h^{-1}, preferably in the range of from 800 to 1200 h^{-1}.

A preferred embodiment (74) concretizing any one of embodiments (60) to (73), further comprising after (III)

(IV) separating the zeolite catalyst or the molding from the reaction zone.

A preferred embodiment (75) concretizing embodiment (74), further comprising after (IV)

(V) recycling the zeolite catalyst or the molding to (I).

A preferred embodiment (76) concretizing embodiment (74) or (75), wherein after (IV) and prior to (V) the zeolite catalyst or the molding is not subject to a step of washing or drying, wherein preferably the zeolite catalyst or the molding is not subject to any treatment after (IV) and prior to (V).

A preferred embodiment (77) concretizing any one of embodiments (60) to (76), wherein the zeolite catalyst or the molding is recycled n times, wherein n is a natural number equal or higher than 1, wherein n preferably ranges from 1 to 100, more preferably from 1 to 75, more preferably from 1 to 50, more preferably from 1 to 20, more preferably from 1 to 10, and more preferably from 1 to 5.

According to an embodiment (78), the present invention further relates a use of a zeolite catalyst according to any one of embodiments (1) to (17) or of a molding according to any one of

embodiments (18) to (25) and (59) as a dehydrogenation catalyst, preferably for the dehydrogenation of one or more alkanes, more preferably for the dehydrogenation of one or more alkanes selected from the group consisting of propane, n-butane, isobutane, n-pentane, isopentane, neopentane, 2-methylpentane, 3-methylpentane, 2,3-dimethylpentane, 2,2-dimethylpentane, n-hexane, and a mixture of two or more thereof, and more preferably for the dehydrogenation of one or more alkanes selected from the group consisting of propane, n-butane, isobutane, and a mixture of two or more thereof.

EXPERIMENTAL SECTION

Example 1: Pt/ZSM-5 catalyst

Example 1 describes the preparation of a Pt/ZSM-5 catalyst. Zeolite ZSM-5 (MFI-type, Si/Al ratio = 850 mole/mole) and hydroxyethylcellulose were mixed and ammonia (25 %) was added. After addition of Ludox AS40 (silica sol), polyethyleneoxide and water 1.5 mm extrudates were formed. The shaped bodies were dried at 120 °C for 3 h and subsequently calcined at 600 °C for 48 h yielding extrusions with 80% zeolite and 20% silica binder. The extrudates were then subjected to an acid treatment. The support was immersed in nitric acid (20 wt.-%) for 1 h and subsequently washed with deionized water until a pH of 5.5 was reached. The treated extrudates were dried at 120 °C for 3 h and calcined at 600 °C for 16 h. The catalyst was prepared by incipient wetness impregnation of the extrusions with an appropriate amount of $Pt(NH_3)_4Cl_2*H_2O$ solution to yield the desired loading of Pt related to the zeolite contained in the shaped bodies. Impregnated extrudates were dried at 40°C in vacuum (25 mbar) for 1h and subsequently dried at 80 °C for 16 h under atmospheric pressure to yield a final metal loading of 0.5 wt.-% Pt related to the zeolite.

Example 2: Pt/ZSM-5 catalyst

Example 2 describes a catalyst prepared similarly with that of Example 1, except that the zeolite extrusions were not treated with nitric acid.

Example 3: Pt/ZSM-5 catalyst

Example 3 describes a catalyst prepared similarly with that of Example 1, except that the Pt load was 0.25 wt% related to the zeolite amount. The zeolite used had a Si/Al ratio of 870 moles/mole.

Example 4: Pt/ZSM-5 catalyst

Example 4 describes a catalyst prepared similarly with that of Example 1, except that the Pt load was 0.125 wt% related to the zeolite amount. The zeolite used had a Si/Al ratio of 870 moles/mole.

Example 5: Pt-Zn/ZSM-5 catalyst

Example 5 describes the preparation of a Pt-Zn/ZSM-5 catalyst. The zeolite (Si/Al ratio = 850 mole/mole) extrusions were prepared as in Example 1, including the acid treatment. The

shaped bodies were loaded with Zn by incipient wetness using an appropriate amount of Zn(C2H3O2)2.2H2O in water. After calcination in air at 550°C for 16 h, the Zn/ZSM-5 extrusions were impregnated with Pt as described in Example 1 to yield a final metal loading of 0.5 wt.-% Pt and 4 wt.-% Zn.

Example 6: Pt-Zn/ZSM-5 catalyst

Example 6 describes a catalyst prepared similarly with that of Example 1, except that the metal loading was 0.5 wt.-% Pt and 1 wt.-% Zn and the zeolite used had a Si/Al ratio of 870 moles/mole.

Example 7: Pt-Zn/ZSM-5 catalyst

Example 7 describes the preparation of a Pt-Zn/ZSM-5 catalyst in form of tablets (binder-free). The zeolite (Si/Al ratio = 3700 mole/mole) was first subjected to an acid treatment. The zeolite powder was immersed in nitric acid (20 wt.-%) for 1 h and subsequently filtered and washed with deionized water until a pH of 5.5 was reached. The zeolite was then dried at 120 °C for 3 h and calcined at 600 °C for 16 h. The powder was then suspended in a solution of Zn(C2H3O2)2.2H2O in water, containing an appropriate amount of salt to yield 4 wt% Zn/ZSM-5. The weight ratio of solution to zeolite was 5:1. The suspension was placed in a rotary evaporator and dried at 40°C in vacuum (25 mbar). The powder was then calcined at 550°C for 16 h. The Zn/ZSM-5 material was suspended in a Pt(NH3)4Cl2*H2O solution (5 fold amount related to the solid material) containing an appropriate amount of salt to yield 0.5 wt.% Pt related to ZSM-5. After drying the suspension at 40°C in vacuum (25 mbar) and subsequently at 80 °C for 16 h under atmospheric pressure a zeolite powder containing 0.5 wt.-% Pt and 4 wt.-% Zn was obtained. This was pressed to pellets using 3% graphite and crushed to a split fraction of 1-2 mm.

Example 8: Pt-Na/ZSM-5 catalyst

Extrudates for example catalyst 8 were prepared according to example 3. A Pt-Na catalyst was prepared via co-impregnation of Pt(NH3)4Cl2*H2O and NaOH. Impregnated extrudates were dried at 40°C in vacuum (25 mbar) for 1h and subsequently dried at 80 °C for 16 h under atmospheric pressure. The catalyst has a final metal loading of 0.5 wt.-% Pt and 1.0 wt.-% Na.

Example 9: Pt-K/ZSM-5 catalyst

Extrudates for example catalyst 9 were prepared according to example 3. A Pt-K catalyst was prepared via co-impregnation of $Pt(NH_3)_4Cl_2*H_2O$ and KOH. Impregnated extrudates were dried at 40°C in vacuum (25 mbar) for 1h and subsequently dried at 80 °C for 16 h under atmospheric pressure. The catalyst has a final metal loading of 0.5 wt.-% Pt and 2.0 wt.-% K.

Example 10: Pt-K/ZSM-5 catalyst

Extrudates for example catalyst 10 were prepared according to example 1. A Pt-K catalyst was prepared via co-impregnation of $Pt(NH_3)_4Cl_2*H_2O$ and KOH. Impregnated extrudates were dried at 40°C in vacuum (25 mbar) for 1h and subsequently dried at 80 °C for 16 h under atmospheric pressure. The catalyst has a final metal loading of 0.5 wt.-% Pt and 0.25 wt.-% K.

Example 11: Pt-Zn-K/ZSM-5 catalyst
Extrudates for example catalyst 11 were prepared according to example 1. A Pt-Zn-K catalyst was prepared by impregnation of $Zn(C_2H_3O_2)_2x2H_2O$. Impregnated extrudates were dried at 40°C in vacuum (25 mbar) for 1h and subsequently dried at 80 °C for 16 h under atmospheric pressure before calcination at 550 °C for 16 h. $Pt(NH_3)_4Cl_2*H_2O$ and KOH were co-impregnated and the catalyst was dried at 40°C in vacuum (25 mbar) for 1h and subsequently dried at 80 °C for 16 h under atmospheric pressure. The catalyst has a final metal loading of 0.5 wt.-% Pt, 4.0 wt.-% Zn and 2.0 wt.-% K.

Example 12: Pt-Zn-K/ZSM-5 catalyst
The catalyst for example 12 was prepared according to example 11, except for the final metal loading being 0.25 wt.-% Pt, 4.0 wt.-% Zn and 0.4 wt.-% K.

Example 13: Pt-Zn-K/ZSM-5 catalyst
The catalyst for example 13 was prepared according to example 11, except for the final metal loading being 0.15 wt.-% Pt, 2.0 wt.-% Zn and 1 wt.-% K.

Example 14: Pt-Zn-K/ZSM-5 catalyst
The catalyst for example 14 was prepared according to example 11, except for the final metal loading being 0.5 wt.-% Pt, 1.0 wt.-% Zn and 0.25 wt.-% K.

Example 15: Pt-Zn-K/ZSM-5 catalyst
The catalyst for example 15 was prepared according to example 11, except for the final metal loading being 0.25 wt.-% Pt, 3.5 wt.-% Zn and 1.5 wt.-% K.

Example 16: Pt-Zn/ZSM-5 catalyst
Extrudates for example 16 were prepared according to example 3. A Pt-K catalyst was prepared via co-impregnation of $Pt(NH_3)_4Cl_2*H_2O$ and $Zn(C_2H_3O_2)_2x2H_2O$. Impregnated extrudates were dried at 40°C in vacuum (25 mbar) for 1h and subsequently dried at 80 °C for 16 h under atmospheric pressure. The catalyst has a final metal loading of 0.5 wt.-% Pt and 0.06 wt.-% Zn.

Example 17: Pt-Zn/ZSM-5 catalyst
The catalyst for example 17 was prepared according to example 16, except for the final metal loading being 0.1 wt.-% Pt and 0.03 wt.% Zn.

Example 18: Pt-Zn/ZSM-5 catalyst
The catalyst for example 18 was prepared according to example 7, except for the final metal loading being 0.5 wt.-% Pt and 0.17 wt.% Zn.

Example 19: Pt-Zn/ZSM-5 catalyst
The catalyst for example 19 was prepared according to example 16, except for the final metal loading being 0.5 wt.-% Pt and 0.25 wt.% Zn.

Example 20: Pt-K/ZSM-5 catalyst
The catalyst for example 20 was prepared according to example 10, except for the final metal loading being 0.5 wt.-% Pt and 2.0 wt.% K.

Example 21: Pt-Zn-K/ZSM-5 catalyst
The catalyst for example 21 was prepared according to example 11, except for the final metal loading being 0.5 wt.-% Pt, 4.0 wt.-% Zn and 2.0 wt.-% K.

Comparative Example 1: Pt/silicalite catalyst
As a comparative example, a catalyst was prepared according to the procedure in example 1 using silicalite instead of ZSM-5. Silicalite is an Al-free microporous silicon dioxide having the same crystalline structure as ZSM-5, i.e. an MFI-type structure, but no acidic centers connected with Al cations in the structure.

Example 21: Catalytic testing - Propane dehydrogenation

Prior to the catalytic test, the samples were calcined and reduced in the catalytic reactor. Generally, the samples were treated in air at 400°C for 4 h then reduced in hydrogen at 530°C for 2 h. Exceptions from this procedure are indicated in Table 2.

Table 1: Overview on the catalysts prepared and their chemical composition.

Catalyst	Content [wt.-%]						Si:Al molar ratio	extrudate/ tablett
	Pt	Zn	K	Na	Si	Al		
Ex. 1	0.50%	0.00%	0.00%	< 0,003%	42.00%	0.0460%	850	extrudate
Ex. 2	0.50%	0.00%	0.00%	< 0.003%	42.00%	0.0460%	850	extrudate
Ex. 3	0.25%	0.00%	0.00%	< 0.003%	42.00%	0.0450%	870	extrudate
Ex. 4	0.125%	0.00%	0.00%	< 0.003%	42.00%	0.0450%	870	extrudate
Ex. 5	0.50%	4.00%	0.00%	< 0.003%	44.00%	0.0460%	850	extrudate
Ex. 6	0.50%	1.00%	0.00%	< 0.003%	42.00%	0.0450%	870	extrudate
Ex. 7	0.50%	4.00%	0.00%	0.0080%	44.00%	0.0110%	3700	tablett
Ex. 10	0.50%	0.00%	0.25%	< 0.003%	44.00%	0.0460%	850	extrudate
Ex. 11	0.50%	4.00%	0.25%	< 0.003%	44.00%	0.0460%	850	extrudate
Ex. 12	0.25%	4.00%	0.40%	< 0.003%	42.00%	0.0450%	870	extrudate
Ex. 13	0.15%	2.00%	1.00%	< 0.003%	42.00%	0.0450%	870	extrudate

Cata-lyst	Content [wt.-%]						Si:Al molar ratio	extrudate/ tablett
	Pt	Zn	K	Na	Si	Al		
Ex. 14	0.50%	1.00%	0.25%	< 0.003%	42.00%	0.0450%	870	extrudate
Ex. 15	0.25%	3.50%	1.50%	< 0.003%	42.00%	0.0450%	870	extrudate
Ex. 16	0.50%	0.06%	0.00%	< 0.003%	42.00%	0.0450%	870	extrudate
Ex. 17	0.10%	0.03%	0.00%	< 0.003%	42.00%	0.0450%	870	extrudate
Ex. 18	0.50%	0.17%	0.00%	< 0.003%	42.00%	0.0450%	870	tablett
Ex. 18	0.50%	0.17%	0.00%	< 0.003%	42.00%	0.0450%	870	tablett
Ex. 19	0.50%	0.25%	0.00%	< 0.003%	42.00%	0.0450%	870	extrudate
Ex. 20	0.50%	0.00%	2.00%	< 0.003%	43.00%	0.0460%	900	extrudate
Ex. 21	0.50%	4.00%	2.00%	< 0.003%	42.00%	0.0460%	870	extrudate
Comp. Ex. 1	0.50%	0.00%	0.00%	0.00%	42.00%	0.00%	Al-free	extrudate

Of the numerous results obtained from catalytic testing under a variety of testing conditions, a selection of representative examples tested under representative conditions are shown in the following Table 2.

Table 2: Catalytic results in propane dehydrogenation (mean values after the first 24 h on stream).

Catalyst	T exit [°C]	Propane conver-sion [%]	Propene Selectivity [%]	Crack Se-lektivity [%]	Propene Yield [%]
Ex. 5	552	22.51	95.53	3.88	21.51
	602	56.46	60.19	39.21	33.86
Ex. 6	553	23.83	93.38	4.92	22.25
	604	47.83	81.50	17.89	38.97
Ex. 10	541	20.40	97.22	2.58	19.84
	601	38.08	88.11	11.88	33.53
Ex. 11	547	22.06	97.55	2.22	21.52
	607	40.90	90.89	9.07	37.17
Ex. 14	546	23.24	96.17	3.46	22.35
	599	41.19	91.73	6.99	37.78
Comp. Ex. 1	602	4.80	56.20	43.80	2.70

Testing conditions of the results in Table 2:

molar ratios of the feed				GHSV C3	p
C3 :	H2	H2O:	N2	(h^{-1}) norm	[bar(abs)]
10	1.0	0.0	1.7	800	1.5

Thus, as may be taken from the results shown in table 2, it has surprisingly been found that catalysts displaying a silicon to aluminum ratio comprised in the range of from 500 to 10,000 display comparatively high propane conversion rates and excellent propene selectivities as well as comparatively low cracking selectivities for affording high yields in the desired propene product. This compares drastically to the use of silicalite as of the zeolite in comparative example 1, which contains no aluminum, and only achieves a very low propane conversion rate in addition to a low propene selectivity and a high cracking selectivity, such as to afford a very low yield in propene. Furthermore, although not reflected in the results shown above, compared to catalysts known in the art displaying substantially lower silicon to aluminum ratios, the inventive catalysts show very little coking and therefore very little deactivation during use thereof. Consequently, it has quite unexpectedly been found that the inventive catalysts display excellent catalytic activities and selectivities yet are not susceptible to coking such that they display surprisingly low rates of deactivation during use.

Example 21: Catalytic testing - Butane dehydrogenation

Catalyst activation

The shaped bodies were tested in C_4 dehydrogenation. Prior to catalytic test the samples were calcined and reduced in-situ. First, the samples were treated in air at 200 °C for 4 h and subsequently reduced in hydrogen at 400 °C for 2 h.

n-butane dehydrogenation

PtZn

n-C4:H2=10:1, 540°C

Cat.	p In bar	n-C4 conversion In %	C-selectivity butenes In %	C-selectivity cracking products In %	C-selectivity isobutane In %	C-selectivity butadiene In %	TOS In h
Ex. 19	1.6	48	82	12	3	3	180
Ex. 19	1.5	49	82	12	3	4	205
Ex. 19	1.4	50	83	12	2	4	250

PtZn

n-C4:H2=20:1, 540°C

Cat.	p In bar	n-C4 conversion In %	C-selectivity butenes In %	C-selectivity cracking products In %	C-selectivity isobutane In %	C-selectivity butadiene In %	TOS In h

Ex. 19	1.4	50	84	11	2	4	275

PtZnK
n-C4:H2=10:1, 535°C

Cat.	p In bar	n-C4 conversion In %	C-selectivity butenes In %	C-selectivity cracking products In %	C-selectivity isobutane In %	C-selectivity butadiene In %	TOS In h
Ex. 21	1.4	41	93	3	<1	4	120

After >300 h TOS the PtZn catalyst showed a deactivation of 0.0094%/h (n-C4:H2=10:1, 540°C). Examples above show that increasing the hydrogen partial pressure is not suitable for the PtZn catalyst since the selectivity to hydrocracking reactions will increase and selectivity to butenes decrease accordingly.

For the PtZnK catalyst a deactivation rate of 0.0444%/h could be observed. Increasing the hydrogen feed concentration (n-C4:H2=1:1) could significantly enhance the stability, which reached a deactivation of <3%/1000h maintaining a selectivity towards butenes of more than 95% after >500 h TOS. Butadiene selectivity decreased by increased H2 partial pressure but hydrogen assisted cracking reactions are suppressed due to suitable promotion of the catalyst and in contrast to the PtZn catalyst.

Isobutane dehydrogenation

i-C4:H_2=10:1

Catalyst	T In °C	i-C4 conversion In %	C-selectivity isobutene In %	C-selectivity cracking products In %	C-selectivity n-butane In %	C-selectivity butadiene In %	TOS In h
Ex. 19 PtZn	542	51	55	10	21	<1	75
Ex. 8 PtNa	525	54	52	26	13	<1	24
Ex. 20 PtK	531	43	58	26	10	<1	24
Ex. 21 PtZnK	535	35	98	2	0	<1	24

PtZnK shows a high selectivity at start of run >98% and after 525 h TOS still >93 % compared to the PtZn catalyst which shows a stable performance after several hundreds of hrs of TOS, however, the selectivity to isobutene is only ~55%.

As can be gathered from the results for experimental testing the inventive examples showed a surprisingly high activity and stability. As shown in the examples, the use of only PtZn or PtK showed lower selectivities and/or stabilities than PtZnK. In isobutane dehydrogenation, a constant

yield was obtained with a remaining selectivity of >93%. In n-butane dehydrogenation the deactivation could be reduced by increasing the hydrogen partial pressure to obtain a deactivation rate of about 2.8%/1000 h. The formation of byproducts as observed for the PtZn catalyst as a consequence of hydrocracking reactions, was not observed, since suitable promotion of the catalyst would prevent side reactions and maintains a high selectivity.

Cited Literature:

- US 5126502 A
- US 7432406 B1
- US 2019/232255 A1
- CN 108579742 A
- CN 104289218 A
- CN 105521813 A
- CN 105582919 A
- WO 2010/076928 A1
- G. J. Siri et al., Materials Letters 2005, 59, 2319-2324
- M. Tasbihi et al., Fuel Processing Technology 2007, 88, 883-889
- J. Camacho-Bunquin et al., ACS Catal. 2018, 8, 10058-10063
- B. Mallanna Nagaraja et al., Catalysis Today 2014, 232, 40-52
- C. Chen et al., Catal. Sci. Technol. 2019, 9, 1979

Claims

1. A zeolite catalyst, wherein the zeolite catalyst comprises a zeolitic material, wherein the framework of the zeolitic material comprises YO_2 and X_2O_3, wherein Y is a tetravalent element and X is a trivalent element, wherein the Y : X molar ratio of Y and X contained in the framework of the zeolitic material is comprised in the range of from 500 to 10,000, and
wherein the zeolite catalyst further comprises Pt which is supported on the zeolitic material.

2. The zeolite catalyst of claim 1, wherein Y is selected from the group consisting of Si, Sn, Ti, Zr, Ge, and a combination of two or more thereof.

3. The zeolite catalyst of claim 1 or 2, wherein X is selected from the group consisting of B, Al, Ga, In, and a combination of two or more thereof.

4. The zeolite catalyst of any one of claims 1 to 3, wherein the zeolitic material has a framework structure containing rings with a maximum ring size of 10 T-atoms.

5. The zeolite catalyst of any one of claims 1 to 4, wherein the zeolite catalyst further comprises Zn, wherein Zn is supported on the zeolitic material.

6. The zeolite catalyst of claim 5, wherein the zeolite catalyst comprises Pt and Zn in elemental form, wherein preferably Pt and Zn form a PtZn alloy.

7. The zeolite catalyst of any one of claims 1 to 6, wherein the zeolite catalyst further comprises one or more metals selected from the group consisting of alkali metals and alkaline earth metals, wherein the one or more metals are respectively supported on the zeolitic material, wherein the one or more metals are preferably selected from the group consisting of Na, K, and Mg, wherein more preferably the zeolite catalyst further comprises K.

8. The zeolite catalyst of claim 7, wherein the zeolite catalyst comprises the one or more metals selected from the group consisting of alkali metals and alkaline earth metals as counter-ion at an ion exchange site of the framework structure.

9. The zeolite catalyst of any one of claims 1 to 8, wherein the Y : X molar ratio of Y and X contained in the framework of the zeolitic material is comprised in the range of from 750 to 6,000, preferably in the range of from 800 to 4,000, and more preferably in the range of from 850 to 3,700.

10. A molding comprising a zeolite catalyst according to any one of claims 1 to 9.

11. The molding of claim 10, wherein the molding further comprises a binder, wherein the binder is selected from the group consisting of silica, alumina, titania, zirconia, magnesia, a silica-alumina mixed oxide, a silica-titania mixed oxide, a silica-zirconia mixed oxide, a silica-lanthana mixed oxide, a silica-zirconia-lanthana mixed oxide, an alumina-titania mixed oxide, an alumina-zirconia mixed oxide, an alumina-lanthana mixed oxide, an alumina-zirconia-lanthana mixed oxide, a titania-zirconia mixed oxide, and a mixture and/or mixed oxide of two or more thereof.

12. A process for the preparation of a molding, preferably of a molding according to claim 10 or 11, wherein the process comprises
(a) preparing a mixture comprising a zeolitic material and optionally a source of a binder;
(b) shaping the mixture obtained from (a); to obtain a precursor molding;
(b') optionally drying of the precursor of the molding in a gas atmosphere
(c) calcining the precursor molding in a gas atmosphere;
(d) subjecting the calcined precursor molding obtained from (c) to one or more impregnation procedures, preferably one or more ion exchange procedures, with a source of Pt, optionally with a source of Zn, and optionally with a source of one or more metals selected from the group consisting of alkali metals and alkaline earth metals, to obtain the molding;
wherein the framework of the zeolitic material comprises YO_2 and X_2O_3, wherein Y is a tetravalent element and X is a trivalent element, and wherein the Y : X molar ratio of Y and X contained in the framework of the zeolitic material is comprised in the range of from 500 to 10,000.

13. A process for the dehydrogenation of one or more alkanes comprising
(I) providing a reactor comprising a reaction zone, wherein the reaction zone comprises a zeolite catalyst according to any one of claims 1 to 9, or a molding according to claim 10 or 11;
(I') optionally subjecting the zeolite catalyst provided in (I) to a reduction treatment
(II) providing a feed comprising one or more alkanes into the reaction zone according to (I) or (I') under reaction conditions in the reaction zone; obtaining a product mixture;
(III) separating the product mixture from the reaction zone.

14. The process of claim 13, wherein the one or more alkanes are selected from the group consisting of propane, n-butane, isobutane, n-pentane, isopentane, neopentane, 2-methylpentane, 3-methylpentane, 2,3-dimethylpentane, 2,2-dimethylpentane, n-hexane, and a mixture of two or more thereof.

15. Use of a zeolite catalyst according to any one of claims 1 to 9 or of a molding according to claim 10 or 11 as a dehydrogenation catalyst.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2021/070267

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01J23/42 B01J23/60 B01J23/58 B01J29/44 B01J37/18
C07C5/333
ADD.
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)
B01J C07C

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 practicable, 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	JP 2002 320857 A (MITSUBISHI RAYON CO) 5 November 2002 (2002-11-05)	1-4,6-15
Y	paragraphs [0018] - [0022], [0027], [0028]; claims 1,3; example 1	5
X	CN 104 107 712 B (CHINA PETROLEUM & CHEMICAL ET AL.) 13 February 2018 (2018-02-13)	1-4,6-15
Y	claim 1; examples 10, 1; table 1	5

-/--

[X] Further documents are listed in the continuation of Box C.

[X] 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 application or patent 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	Date of mailing of the international search report
16 October 2021	27/10/2021

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Beckmann, Oliver

1

Form PCT/ISA/210 (second sheet) (April 2005)

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	CHEN CHONG ET AL: "ZnO supported on high-silica HZSM-5 as efficient catalysts for direct dehydrogenation of propane to propylene", MOLECULAR CATALYSIS, vol. 476, 17 July 2019 (2019-07-17), page 110508, XP055851768, ISSN: 2468-8231, DOI: 10.1016/j.mcat.2019.110508 page 1, left-hand column, paragraph 2 -----	5

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2021/070267

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 2002320857 A	05-11-2002	NONE	
CN 104107712 B	13-02-2018	NONE	