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(54) Title: Catalyst for the Conversion of Syngas to Olefins and Preparation Thereof

(57) Abstract: The present invention relates to a process for the production of a pillared silicate comprising: (i) providing a layered silicate; (ii)interlayer expanding the layered silicate provided in step (i) comprising a step of treating the layered silicate with one or more swelling agents; (iii)treating the interlayer expanded silicate obtained in step (ii) with one or more hydrolyzable silicon containing compounds; (iv)treating the interlayer expanded compound obtained in step (iii) with an aqueous solution to obtain a pillared silicate; (v)removing at least a portion of the one or more swelling agents from the pillared silicate obtained in step (iv); (vi) impregnating the pillared silicate obtained in step (v) with one or more elements selected from the group consisting of Fe, Ru, Ir, and combinations of two or more thereof, as well as to a pillared silicate optionally obtainable from said process and its use, in particular in a process for the production of one or more olefins according to the invention.

Catalyst for the Conversion of Syngas to Olefins and Preparation Thereof

The present invention relates to a process for the production of a pillared silicate compound as well as to a pillared silicate compound obtainable from such a process. Furthermore, the present invention relates to a pillared silicate compound *per se* as well as to a process for the production of one or more olefins using the aforementioned pillared silicate compounds. Finally, the present invention also relates to the use of the aforementioned pillared silicate compounds.

INTRODUCTION

In the field of catalysis, as well as in the field of processes involving adsorption and/or absorption of chemical compounds, providing novel framework topologies with novel pore architectures plays a crucial role in the development of catalysts, catalyst components, and catalyst support materials displaying novel reactivity and/or improved performance. In this respect, besides efforts which have been invested into creating novel three-dimensional zeolitic frameworks from organotemplate-mediated selforganization processes as may for example be achieved in hydrothermal synthetic procedures, efforts have been made to create micro- and/or macroporous structures starting from layered materials and in particular layered silicates by chemical bonding of the layers with one another thus affording three-dimensional frameworks. In this respect, the condensation of layered silicates into new zeolitic frameworks via topotactic procedures may be mentioned. For achieving greater degrees of interlayer expansion, methods may also be mentioned wherein pillaring agents are introduced into layered materials. In this respect, it has been found that the use of auxiliary agents which are intercalated between the layers and later at least in part removed from the pillared materials may be employed for achieving greater degrees of interlayer expansion.

Thus, as regards the aforementioned methods, the synthesis and characterization of products resulting from the reaction of selected layered silicates having the MWW, FER, CDO, and MCM-47 topologies with diethoxydimethyl silane as disclosed in P. Wu et al., *J. Am. Chem. Soc.* **2008**, vol. 130, pp. 8178-8187 may be mentioned.

EP 0 626 200 A1, on the other hand, relates to the production of silica-pillared micas which may be produced by intercalating an organosilicon oligomer/precursor into a layered fluoromica, followed by calcination thereof. WO 2010/100191 A1, on the other hand, discloses a process for the preparation of pillared silicates employing hydrothermal conditions. Besides these, O.-Y. Kwon et al., *Bull. Korean Chem. Soc.* **1999**, vol. 20, pp. 69-75, concerns silica-pillared H-kenyaites produced by interlamellar base catalyzedreaction of tetraethylorthosilicate wherein the intercalation of tetraethylorthosilicate is conducted with the aid of octylamine employed in a pre-swelling process.

Despite the results which have been achieved for obtaining interlayer expanded three-dimensional structures from such pillaring processes, there remains the need for novel structures and materials displaying unprecedented chemical properties and reactivities for use in various applications and in particular for use in the increasingly important field of catalysis and in particular of heterogeneous catalysis in which microporous structures such as those found in zeolitic materials have found a very large number of applications.

DETAILED DESCRIPTION

It is therefore the object of the present invention to provide a novel process for the preparation of interlayer expanded layered silicates, i.e. pillared layered silicates. In particular, it is the object of the present invention to provide novel zeolitic-type frameworks with expanded pore openings displaying improved physical and chemical properties in particular in the field of heterogeneous catalysis.

Thus, it has quite surprisingly been found that a specific pillaring of silicates may afford interlayer expanded structures with highly defined micro- and/or mesoporous frameworks displaying unprecedented physical properties in particular with respect to the surface areas which may be achieved in the resulting materials. Furthermore, it has quite unexpectedly been found that the incorporation of specific catalytically active metal species into the novel framework structures afford improved catalytic activities which clearly outperform microporous materials commonly used in the art as a support for such catalytically active metals. Even more surprisingly, however, it has been found that the interlayer expanded materials according to the present invention may accommodate novel species of the catalytically active metals and in particular metal clusters species which may not be generated in their microporous counterparts. Finally, it has quite unepxectedly been found that the inventive interlayer expanded materials, and in particular those containing specific catalytically active components and in particular specific metals, display improved catalytic activities and selectivities compared to their microporous counterparts when used as the catalytic support material.

Thus, the present invention relates to a process for the production of a pillared silicate compound comprising

- (i) providing a layered silicate;
- (ii) interlayer expanding the layered silicate provided in step (i) comprising a step of treating the layered silicate with one or more swelling agents;

(iii) treating the interlayer expanded silicate obtained in step (ii) with one or more hydrolyzable silicon containing compounds;
(iv) treating the interlayer expanded compound obtained in step (iii) with an aqueous solution to obtain a pillared silicate;
(v) removing at least a portion of the one or more swelling agents from the pillared silicate obtained in step (iv);
(vi) impregnating the pillared silicate obtained in step (v) with one or more elements selected from the group consisting of Fe, Ru, Ir, and combinations of two or more thereof.

Concerning the layered silicate compound which is provided in step (i), there is no particular restriction according to the present invention as to the type of compound which may be used in this respect provided that it may be interlayer expanded when treated with a swelling agent in step (ii), and that it comprises chemical functionalities which under suitably chosen reaction conditions may react with a hydrolyzable silicon containing compound in steps (iv) and/or (v) for affording a pillared silicate compound.

Thus, in principle, any suitable layered silicate may be employed in the inventive process, wherein the layered silicate provided in step (i) may comprise one or more layered silicate compounds. Preferably, the one or more silicate compounds provided as layered silicate in step (i) are selected from the group consisting of MCM-22, PREFER, Nu-6(2), CDS-1, PLS-1, MCM-47, ERS-12, MCM-65, RUB-15, RUB-18, RUB-20, RUB-36, RUB-38, RUB-39, RUB-40, RUB-42, RUB-51, BLS-1, BLS-3, ZSM-52, ZSM-55, kanemite, makatite, magadiite, kenyaite, revdite, montmorillonite, and mixtures of two or more thereof. According to particularly preferred embodiments of the present invention, the layered silicate provided in step (i) comprises RUB-36 and/or RUB-39, wherein it is yet further preferred that the layered silicate provided in step (i) is RUB-36.

Layered silicates of the structure type RUB-36 are known in the art. For example, reference is made to the all-silica RUB-36 layered silicate consisting of Si and O, described in J. Song, H. Gies, *Studies in Surface Science and Catalysis* **2004**, vol. 15, pp. 295-300, the contents of which are incorporated herein by reference. According to the present invention, the RUB-36 layered silicate is preferably defined as a compound having an X-ray diffraction pattern comprising at least the following reflections:

Diffraction angle 2θ/° [Cu K(alpha 1)]	Intensity (%)
7.85 – 8.05	100.0
17.04 – 17.24	1.6 – 5.6
20.26 – 20.46	1.7 – 5.7
23.89 – 24.09	4.2 – 12.2
24.73 – 24.93	4.8 – 12.8

25.30 – 25.50	2.6 – 6.6
26.52 – 26.72	0.7 – 4.7

wherein 100 % relates to the intensity of the maximum peak in the X-ray diffraction pattern.

The precursor layered silicate RUB-39 according to the present invention is defined as a compound having having an X-ray diffraction pattern comprising at least the following reflections:

Diffraction angle 2θ/° [Cu K(alpha 1)]	Intensity (%)
8.15 – 8.35	100.0
16.39 – 16.59	2 – 12
19.87 – 20.07	7 - 17
23.41 – 23.61	9 – 19
29.94 – 30.14	1 - 11
35.90 – 36.10	0.5 - 10

wherein 100% relates to the intensity of the maximum peak in the X-ray diffraction pattern.

As to possible processes for the preparation of RUB-39 silicates, reference is made to WO2005/100242 A1, in particular examples 1 and 2 on pages 32 and 33; WO 2007/042531 A1, in particular example 1 on page 38, example 2 on page 39, example 3 on page 40, example 6 on page 41, and example 7 on page 42; or WO 2008/122579 A2, in particular example 1 on page 36 and example 3 on page 37.

The preparation of the layered silicate RUB-15 is disclosed, for example, in Oberhagemann, U., P. Bayat, B. Marler, H. Gies, and J. Rius in *Angewandte Chemie, Intern. Ed. Engl.* 1996, Vol. 35, No. 23/24, pp. 2869-2872.

As regards the preparation and characterization of the layered silicates BLS-1 and BLS-3, reference is made to WO 2010/100191 A1, the contents of which are incorporated herein by reference.

According to the present invention it is preferred that the layered silicate provided in step (i) is isomorphously substituted. Within the meaning of the present invention, the term “isomorphously substituted” generally refers to compounds having a two- or three-dimensional framework structure and in particular to silicate compounds or zeolitic materials containing silicon, wherein one or more of the framework elements and in particular silicon is substituted by one or more elements, as a result of which positions in the aforementioned framework which would normally be occupied by silicon are in fact occupied by one or more elements other than silicon.

According to said preferred embodiments of the present invention, there is in principle no particular restriction neither with respect to the amount of the one or more elements nor with respect to the type of the one or more elements by which the layered silicate and in particular silicon contained in the layered silicate is isomorphously substituted provided that a pillared silicate may be obtained according to the inventive process. It is, however, preferred that the one or more elements by which the layered silicate provided in step (i) is isomorphously substituted is selected from the group consisting of Al, B, Fe, Ti, Sn, Ga, Ge, Zr, V, Nb, Zn, Li, Be and mixtures of two or more thereof. According to embodiments which are yet further preferred, the layered silicate provided in step (i) is isomorphously substituted by one or more elements selected from the group consisting of Al, B, Fe, Ti, Sn, Zr, and mixtures of two or more thereof, wherein even more preferably the one or more elements are selected from the group consisting of Al, Ti, B, and mixtures of two or more thereof. According to particularly preferred embodiments of the present invention, the layered silicate provided in step (i) is isomorphously substituted with Al and/or Ti, wherein particularly preferably the layered silicate is isomorphously substituted with Al.

Therefore, embodiments of the inventive process for the production of a pillared silicate are preferred, wherein the layered silicate provided in step (i) is isomorphously substituted, preferably with one or more elements selected from the group consisting of Al, B, Fe, Ti, Sn, Ga, Ge, Zr, V, Nb, Zn, Li, Be and mixtures of two or more thereof.

According to the inventive process, the layered silicate provided in step (i) is interlayer expanded in step (ii) using one or more swelling agents. As regards the swelling agents which may be employed in the inventive process, no particular restriction applies neither with respect to the type of the one or more swelling agents which may be used nor with respect to the amount in which they are employed provided that a suitably expanded layered silicate is obtained form the interlayer expanding step. Preferred swelling agents which may be used according to the present invention include surfactants and in particular cationic surfactants which when contacted with the layered silicate penetrate between the individual silicate layers in an ordered fashion for providing a swollen layered structure with an accordingly expanded interlayer spacing compared to the initial layered silicate provided in step (i). Thus, by way of example, any suitable swelling agent may be used for this purpose either alone or in combination with one or more further swelling agents.

According to preferred embodiments of the inventive process, the one or more swelling agents comprise one or more compounds selected from the group consisting of cationic surfactants. As the preferred cationic surfactant used in the inventive process, again any suitable one or more cationic surfactants may be used for interlayer expanding the layered silicate. Thus, by way of example, the one or more swelling agents used in step (ii) may comprise one or more cationic surfactants selected from the group consisting of octenidine dihydrochloride, quaternary ammonium cations and salts thereof, alkyltrimethylammonium salts such as cetyl trimethylammonium bromide (CTAB; hexadecyl trimethyl ammonium bromide), cetyl trimethylammonium chloride (CTAC), cetylpyridinium chloride (CPC), polyethoxylated tallow amine (POEA), benzalkonium chloride (BAC), benzethonium chloride (BZT), 5-Bromo-5-nitro-1,3-dioxane, dimethyldioctadecylammonium chloride, dioctadecyldimethylammonium bromide (DODAB), including combinations of two or more thereof.

According to the present invention it is however preferred that the one or more swelling agents comprise one or more cationic surfactants containing one or more alkyl chains and preferably one or more alkyl chains having four C-atoms or more. Even more preferably, the one or more preferred cationic surfactants contain one to four alkyl chains having four C-atoms or more, wherein even more preferably the cationic surfactant contains one to three alkyl chains having four C-atoms or more, and even more preferably one or two alkyl chains having four C-atoms or more. According to particularly preferred embodiments wherein the one or more swelling agents comprise one or more cationic surfactants containing one or more alkyl chains having four C-atoms or more, the cationic surfactant contains one alkyl chain having four C-atoms or more. As regards the alkyl chain having four C-atoms or more in the cationic surfactant according to the particular and preferred embodiments of the present invention in this respect, there is in principle no particular restriction as to the length which said one to four alkyl chains having four C-atoms or more may have. Thus, by way of example, the one or more alkyl chains having four C-atoms or more may include one or more C_4-C_{26} alkyl chains, wherein preferably the one or more alkyl chains include one or more C_6-C_{24} alkyl chains, more preferably one or more C_8-C_{22} alkyl chains, more preferably of C_{10}-C_{20} alkyl chains, more preferably of C_{12}-C_{18} alkyl chains, more preferably of C_{14}-C_{18} alkyl chains, more preferably of C_{15}-C_{17} alkyl chains. According to particularly preferred embodiments, the one or more alkyl chains having four C-atoms or more include one or more C_{16} alkyl chains.

Therefore, embodiments of the inventive process for the production of a pillared silicate are preferred, wherein the one or more swelling agents used in step (ii) comprise one or more compounds selected from the group consisting of cationic surfactants, wherein the one or more swelling agents preferably comprise one or more cationic surfactants containing one or more alkyl chains having 4 C-atoms or more, wherein more preferably the cationic surfactant contains 1 to 4 alkyl chains having 4 C-atoms or more, the one or more alkyl chains having 4 C-atoms or more preferably including one or more C_4-C_{26} alkyl chains.

According to the present invention it is however particularly preferred that the cationic surfactant comprises one or more tetraalkylammonium compounds. As regards the length of the alkyl chains of the tetraalkylammonium cations in said compounds, there is no particular restriction neither with respect to their respective length, nor with respect to their further characteristics such as whether they may be substituted and/or whether the individual alkyl moieties are respectively branched, provided that interlayer expansion of the layered silicate by action of the tetraalkylammonium compound either by itself or in combination with one or more further swelling agents may be achieved. According to preferred embodiment wherein one or more tetraalkylammonium compounds are employed, it is however preferred that said one or more tetraalkylammonium compounds comprise one or more compounds selected from the group consisting of alkyltrimethylammonium compounds, alkylethyldimethylammonium compounds, alkyldiethylmethylammonium compounds, alkyltriethylammonium compounds, and combinations of two or more thereof. According to yet further preferred embodiments, the one or more swelling agents employed in step (ii) comprise one or more tetraalkylammonium compounds selected from the group consisting of alkyltrimethylammonium compounds, alkylethyldimethylammonium compounds, and combinations of two or more thereof, wherein even more preferably one or more alkyltrimethylammonium compounds are comprised in said one or more swelling agents.

As regards the preferred alkyltrimethylammonium compounds, alkylethyldimethylammonium compounds, alkyldiethylmethylammonium compounds, and/or alkyltriethylammonium compounds comprised in the swelling agents, there is again no particular restriction as to the alkyl group contained in said compounds, neither with respect to the chain length, nor with respect to any substitution and/or branching thereof. Thus, by way of example, the alkyl group of the aforementioned preferred cationic surfactants comprised in the one or more swelling agents employed in step (ii), the alkyl group may be selected from the group consisting of C_4-C_{26} alkyl chains, and more preferably from the group consisting of of C_6-C_{24} alkyl chains, more preferably of C_8-C_{22} alkyl chains, more preferably of C_{10}-C_{20} alkyl chains, more preferably of C_{12}-C_{18} alkyl chains, more preferably of C_{14}-C_{18} alkyl chains, more preferably of C_{15}-C_{17} alkyl chains, and wherein more preferably the alkyl group is a C_{16} alkyl chain, wherein even more preferably the one or more tetraalkylammonium compounds comprises a cetyltrimethylammonium compound.

Therefore, embodiments of the inventive process for the production of a pillared silicate are preferred, wherein the cationic surfactant comprises one or more tetraalkylammonium compounds, preferably one or more tetraalkylammonium compounds selected from the group consisting of alkyltrimethylammonium compounds, alkylethyldimethylammonium compounds, alkyldiethylmethylammonium compounds, alkyltriethylammonium compounds, and combinations of two or more thereof, wherein the alkyl group of the alkyltrimethylammonium compounds, alkylethyldimethylammonium compounds, alkyldiethylmethylammonium compounds, and/or of the alkyltriethylammonium compounds is preferably selected from the group consisting of C_4-C_{26} alkyl chains.

Concerning the preferred and particularly preferred cationic surfactants which may be used in the inventive process as one or more of the swelling agents, there is equally no particular restriction as to the counterions which they may contain, provided that they allow for the swelling of the layered silicate when employed in step (ii) of the inventive process. Thus, by way of example, the counterions to the preferred cationic surfactants according to the particular and preferred embodiments of the present invention may be selected from the group consisting of halides, hydroxides, carboxylates, nitrates, nitrites sulfates, and combinations and/or mixtures of two or more thereof, wherein it is preferred that the counterions are selected from the group consisting of fluoride, chloride, bromide, hydroxides, nitrates, and combinations and/or mixtures of two or more thereof, more preferably from the group consisting of chloride, bromide, hydroxide and combinations of two or more thereof, wherein it is particularly preferred that the counterions of the cationic surfactant according to the particularly preferred embodiments of the present invention comprise bromide.

According to an alternative embodiment of the present invention which is further preferred, in addition to one or more of the preferred tetraalkylammonium cations comprised in the one or more swelling agents as defined in the particular or preferred embodiments described in the present application, a tetraalkylammonium compound wherein the alkyl chains have three C-atoms or less, respectively, is employed in step (ii) of the inventive process. As regards the one or more tetraalkylammonium cations having three C-atoms or less, it is further preferred that said one or more tetraalkylammonium compounds are selected from the group consisting of triethyl-N-propylammonium compounds, diethyldi-N-propylammonium compounds, ethyltri-N-propylammonium compounds, tetra-N-propylammonium compounds, tetraethylammonium compounds, and combinations of two or more thereof, wherein more preferably the one or more tetraalkylammonium compounds comprise one or more tetra-N-propylammonium compounds. According to particularly preferred embodiments of the inventive process, one or more tetra-N-propylammonium compounds are further used in step (ii) together with the one or more swelling agents for the interlayer expansion of the layered silicate provided in step (i).

As regards the counterions to the one or more tetraalkylammonium compounds having alkyl chains of three C-atoms or less according to particular and preferred embodiments of the inventive process, there is again no particular restriction in this respect provided that interlayer expansion of the layered silicate compound may be achieved in step (ii) of the inventive process. Thus, by way of example, the counterions to said one or more tetraalkylammonium cations having alkyl chains of three C-atoms or less are selected from the group consisting of halides, hydroxide, carboxylates, nitrate, nitrite, sulfate, and combinations and/or mixtures of two or more thereof, wherein preferably the counterions are selected from the group consisting of chloride, bromide, hydroxide, and combinations of two or more thereof, wherein even more preferably one or more tetraalkylammonium hydroxides with alkyl chains having three C-atoms or less are employed in addition to the one or more swelling agents in step (ii) of the inventive process.

Concerning the mode in which the interlayer expanding of the layered silicate is realized in step (ii) of the inventive process, there is in principle no particular restriction relative to the procedure which is employed to this effect nor with respect to any further agents or components which may be employed. According to preferred embodiments of the present invention, however, the interlayer expansion conducted in step (ii) is preformed in a solvent system, wherein preferably the one or more swelling agents and according to alternatively preferred embodiments of the inventive process the one or more tetraalkylammonium compounds having alkyl chains with three C-atoms or less are dissolved in said solvent system. According to particularly preferred embodiments thereof, the solvent system comprises one or more solvents comprising water, wherein more preferably the solvent system preferably employed in step (ii) according to particularly and preferred embodiments of the inventive process is water.

With respect to the further treatment of the interlayer expanded layered silicate with one or more hydrolyzable silicon containing compounds, it is preferred according to the present invention that the interlayer expanded silicate to be treated is provided in a substantially water-free state. Within the meaning of the present invention, the term “substantially water-free” refers to a state of the interlayer expanded silicate after it has been subject to a dehydration treatment for achieving a certain state of dryness depending on the layered silicate which is employed as well as the one or more swelling agents comprised therein and on the type of duration of the dehydration treatment which is employed. Thus, according to said preferred embodiments of the inventive process, there is, in principle, no particular restriction as to the type and/or duration of a dehydration treatment which may be conducted prior to step (iii) provided that a dehydrated interlayer expanded silicate may be obtained which is suited for producing a pillared silicate compound when further employed in the inventive process.

By way of example, the interlayer expanded silicate obtained in step (ii) may therefore be subject to any heating treatment for removing, i.e. for reducing the water content in said compound, and/or reduced pressure may be applied to the compound to the same effect. According to particularly preferred embodiments of the present invention, a heat treatment is combined with applying reduced pressure to the interlayer expanded layered silicate obtained from step (ii) for dehydration thereof. As regards the heat treatment which is preferably applied to the interlayer expanded silicate for dehydration thereof, any suitable temperature may be applied for any suitable period of time to this effect. Thus, by way of example, the interlayer expanded silicate obtained in step (ii) may be heated to a temperature in the range of from 35 to 150 °C for removing water therefrom, wherein preferably, the interlayer expanded silicate is heated to a temperature ranging from 40 to 100 °C, more preferably from 45 to 80 °C, more preferably from 50 to 70 °C, and more preferably from 55 to 65 °C. Regarding the duration of the preferred heat treatment, again any suitable period may be chosen for the heat treatment wherein a duration in the range of 0,25 to 24 h is preferred, and more preferably a duration ranging from 0,5 to 10 h, more preferable from 1 to 5 h, and even more preferably from 1,5 to 3 h.

Finally, concerning the preferred application of reduced pressure to the interlayer expanded layered silicate prior to step (iii) of the inventive process, and preferably in combination with a heat treatment according to particular and preferred embodiments of the present invention, there is no particular restriction relative to the vacuum applied provided that it is effective for further reducing the water content of the interlayer expanded silicate, wherein preferably vacuum in the range of anywhere from 3 kPa to 100 nPa may be applied, wherein more preferably vacuum in the range of from 1 kPa to 1 µPa is applied, more preferably of from 100 Pa to 100 µPa, more preferably of from 10 Pa to 1 mPa, and more preferably of from 1 Pa to 100 mPa.

Therefore, embodiments of the inventive process for the production of a pillared silicate compound are further preferred, wherein the interlayer expanded silicate obtained in step (ii) is dehydrated prior to step (iii).

In step (iii) of the inventive process, the interlayer expanded silicate compound obtained in step (ii), which has preferably been dehydrated subsequent to the interlayer expansion conducted in step (ii), is treated with one or more hydrolyzable silicon containing compounds. As regards the one or more hydrolyzable silicon containing compounds which may be employed according to the present invention, any suitable compounds may be employed provided that they may be hydrolyzed in the subsequent treatment step (iv) for achieving hydrolysis thereof. According to preferred embodiments of the present invention, the hydrolyzable silicon containing compound comprises one or more silicon compounds $X^1X^2SiX^3X^4$, wherein X^1, X^2, X^3, and X^4 independently from one another stand for a leaving group, and in particular for a leaving group which is sensitive to hydrolysis and more specifically to hydrolysis as conducted according to particular and preferred embodiments of step (iv) of the inventive process. Thus, by way of example, the leaving group X^1, X^2, X^3, and X^4, which may be the same or different from one another, are preferably selected form the group consisting of hydrogen, halogen and C_1-C_3 alkoxy, wherein more preferably the leaving group is selected from the group of hydrogen, chlorine, bromine, and C_1 and C_2 alkoxy. According to particularly preferred embodiments of the inventive process, the leaving group X^1, X^2, X^3, and X^4 are independently from one another selected from the group consisting of hydrogen, ethoxy, methoxy, and chlorine, wherein even more preferably the leaving group is ethoxy or methoxy. According to particularly preferred embodiments thereof, the hydrolyzable silicon containing compound employed in step (iii) of the inventive process is tetraethoxysilane.

Therefore, embodiments of the inventive process for the production of a pillared silicate compound are preferred, wherein the hydrolyzable silicon containing compound comprises one or more silicon compounds $X^1X^2SiX^3X^4$ wherein X^1, X^2, X^3, and X^4 independently from one another stand for a leaving group, wherein the leaving group X^1, X^2, X^3, and X^4 may be the same or different from one another.

With respect to the treatment of the interlayer expanded silicate in step (iii) with the one or more hydrolyzable silicon containing compounds, there is no particular restriction as to how the treatment is conducted provided that the treated interlayer expanded compound may afford a pillared silicate after the treatment according to step (iv) of the inventive process. Thus, any suitable means may be applied for achieving the treatment in step (iii) both with respect to the conditions used for said treatment as well as with respect to the type and amount of the one or more hydrolyzable silicon containing compounds and the amounts in which it is used. By way of example, the treatment may therefore be achieved by contacting the interlayer expanded silicate with an excess of the one or more hydrolyzable silicon containing compounds relative to the amount of said compounds which may be incorporated into the interlayer expanded silicate at most. As concerns the temperature at which said contacting may be performed, any suitable temperature may be chosen wherein temperatures comprised in the range of 25 °C to the refluxing temperature of the hydrolyzable silicon containing compound in the mixture provided in step (iii) may be chosen wherein preferably the temperature is comprised in the range of from 40 °C to the refluxing temperature, more preferably of from 50 °C to the refluxing temperature, more preferably of from 60 °C to the refluxing temperature, more preferably of from 70 °C to the refluxing temperature, wherein even more preferably the reaction in step (iii) is conducted under refluxing of the hydrolizable silicon containing compound in the mixture provided in step (iii).

Therefore, embodiments of the inventive process for the production of a pillared silicate compound are preferred, wherein in step (iii) the treatment is conducted at a temperature comprised in the range of from 25°C to the refluxing temperature of the hydrolizable silicon containing compound in the mixture provided in step (iii).

Furthermore, as regards the duration of the treatment conducted in step (iii) of the inventive process, said duration may range anywhere from 1 to 72 h, wherein preferably the treatment in step (iii) is conducted for a period of from 8 to 48 h, more preferably of from 12 to 36 h, more preferably of from 16 to 32 h, more preferably of from 20 to 28 h, and even more preferably of from 22 to 26 h.

For avoiding the generation of unnecessary hydrolysis products stemming from the hydrolyzable silicon containing compounds, the treated interlayer expanded compound obtained in step (iii) is preferably dried prior to the treatment in step (iv), wherein said drying treatment is preferably performed at room temperature. In particular, said drying treatment is preferably not performed with the aid of any heating means and/or the application of reduced pressure for avoiding that any of the hydrolyzable silicon containing compounds that are not in excess but rather contained within the interlayer expanded structure and which are the precursors to the pillaring structure obtained in step (iv) be removed from the interlayer expanded silicate treated to this effect in step (iii) of the inventive process.

After having been subject to a treatment with one or more hydrolyzable silicon containing compounds according to any one of the particular or preferred embodiments relative to step (iii) of the present invention, the treated interlayer expanded compound obtained therefrom is then treated with an aqueous solution for obtaining a pillared silicate. In particular, step (iv) of the inventive process allows for the hydrolysis of the one or more hydrolyzable silicon compounds as a result of which silica pillars are formed in-between the layers of the expanded structure. To this effect, any suitable aqueous solution may be employed, although it is preferred to use an aqueous solution having a pH of from 5 to 10 to this effect. According to particularly preferred embodiments of the inventive process, the aqueous solution used in step (iv) has a pH of from 7 to 9, and even more preferably of from 7.5 to 8.5 for achieving a suitable degree of hydrolysis of the hydrolyzable silicon containing compounds contained in the interlayer expanded silicate. For obtaining a solution displaying one of the particular or preferred pH values according to preferred embodiments of the inventive process, any suitable acid and/or base may be employed to this effect, wherein preferably a Bronsted acid and/or base is used to this effect. As concerns the Bronsted bases which are preferably employed in particular for obtaining aqueous solutions of a basic pH ≥ 7, it is particularly preferred that an alkaline metal hydroxide is used to this effect, more preferably sodium and/or potassium hydroxide, and even more preferably sodium hydroxide.

As regards step (v) of the inventive process wherein at least a portion of the one or more swelling agents from the pillared silicate obtained in step (iv) is removed, any suitable means may be employed according to the present invention to this effect. Thus, by way of example, said removal may at least in part be achieved by dissolution of the swelling agent by means of using an appropriate solvent with which one or more of the swelling agents may be washed out of the pillared silicate structure. According to preferred embodiments of the present invention wherein one or more cationic surfactants are comprised among the one or more swelling agents, said dissolution is preferably accompanied by an ion exchange procedure performed before or during the contacting with one or more of the suitable solvents, wherein in the latter case, the ions suited for ion exchange of the one or more cationic surfactants are accordingly dissolved in the solvent used to this effect. More specifically, in cases wherein an ion exchange procedure is used for removing at least a portion of the one or more cationic surfactants, any suitable cation may be used to this effect wherein the pillared silicate compound is preferably treated with a Bronsted acid for exchanging at least part of the one or more cationic surfactants against H^+ ions. Alternatively or in addition thereto, one or more alkaline metal containing salts may be employed which may be dissolved in the solvent which is employed for said ion exchange process for accordingly replacing at least a portion of said one or more cationic surfactants against one or more alkaline metal ions, preferably against sodium and/or potassium, and more preferably against sodium. Instead of or in combination with any one or more of the aforementioned preferred cations which may be used for the ion exchange procedure, one or more ammonium containing salts may be employed in the ion exchange procedure for accordingly substituting at least a portion of the cationic surfactants contained in the pillared silicate compound obtained in step (iii).

According to the present invention it is however preferred that at least a portion of the one or more swelling agents is removed from the pillared silicate by degradation of said one or more swelling agents wherein said one or more swelling agents dissociate and/or decompose by any suitable physical and/or chemical means into smaller chemical compounds which may easily be removed from the pillared silicate structure either by suitable washing out thereof and/or by diffusion thereof out of the pillared silicate structure such as in the case of gaseous products formed during the degradation procedure. For achieving said preferred degradation, any suitable means may again be employed such as degradation by solvolysis, by irradiation of the one or more swelling agents with a low wavelength source such as an ultraviolet source or higher energy radiation than ultraviolet rays, or by thermolysis, wherein according to the present invention the one or more swelling agents are preferably removed by thermolysis.

As regards the temperature employed according to preferred embodiments wherein the one or more swelling agents are removed by thermolysis, no particular restriction applies such that any suitable temperature may be used. Thus, by way of example, the degradation of the one or more swelling agents may be achieved in step (v) by calcination wherein preferably the calcination temperature is comprised in the range of 250 to 850 °C, more preferably from 350 to 800 °C, more preferably from 400 to 750 °C, more preferably from 450 to 650 °C, more preferably from 500 to 600 °C, and even more preferably from 525 to 575 °C. According to said particularly preferred embodiments wherein the one or more swelling agents which are at least partly removed from the pillared silicate obtained in step (iv) is removed by calcination, it is preferred that the one or more swelling agents are chosen such that the calcination and in particular the calcination performed at temperatures according to the particular or preferred embodiments of the present invention leads to the formation of gas phase products which accordingly diffuse out of the pillared silicate structure, and in particular to the formation of gas phase products which are formed in the presence of oxygen contained in the atmosphere used for the preferred calcination procedure.

Therefore, embodiments of the inventive process for the production of a pillared silicate are further preferred, wherein step (v) includes a calcination step for removing at least a portion of the swelling agent.

Finally, in step (vi) of the inventive process, the pillared silicate obtained in step (v) is impregnated with one or more elements selected from the group consisting of iron, ruthenium, iridium, and combinations of any two or more thereof. As regards the impregnation procedure which may be used for achieving the loading of the pillared silicate obtained in step (v) with one or more of the aforementioned elements, any suitable procedure may be used wherein one or more of the aforementioned elements is introduced into the micro- and/or mesoporous structure of the pillared silicate obtained in step (v), either as the element such as in colloidal and/or nanodisperse form or as a salt of one or more of the aforementioned elements. As regards embodiments wherein the one or more elements selected from the group consisting of Fe, Ru, Ir, and combinations of two or more thereof is introduced into the pillared silicate structure in ionic form, it is particularly preferred according to the present invention that said one or more elements are introduced in the form of a metal complex and/or organometallic compound, and in particular in the form of a metal complex.

Therefore, according to preferred embodiments of the inventive process, the one or more sources for the one or more elements in step (vi) comprises one or more metal compounds selected from the group consisting of metal salts, metal complexes, organometallic compounds, and combinations of two or more thereof, wherein preferably the one or more metal compounds comprise one or more organometallic compounds and/or metal complexes, wherein even more preferably the one or more metal compounds comprise one or more metal complexes.

As regards the metal salts which are employed as the one or more sources of the one or more elements in step (vi) according to particular embodiments of the inventive process, any suitable salt or salt mixtures may be employed provided that they may be effectively impregnated into the pillared silicate structure. Thus, by way of example, said one or more metal salts may comprise one or more compounds selected form the group consisting metal halides, metal hydroxides, metal carbonates, metal carboxylates, metal nitrates, metal nitrites, metal phosphates, metal phosphites, metal phosphonates, metal phosphinates, metal sulfates, metal sulfites, metal sulfonates, metal alkoxides, and combinations of two or more thereof, preferably from the group consisting of metal halides, metal nitrates, metal nitrites, metal sulfates, metal sulfites, and combinations of two or more thereof,more preferably from the group consisting of metal halides, metal nitrates, metal sulfates, and combinations of two or more thereof, more preferably from the group consisting of metal nitrates and/or metal sulfates, wherein more preferably the metal salts comprise one or more metal nitrates.

As regards the particularly preferred embodiments of the present invention wherein the one or more sources for the one or more elements in step (vi) comprise one or more metal complexes, there is no particular restriction according to the inventive process as to the ligands contained in the preferred metal complexes such that, by way of example, these may be selected from the group consisting of mono-, bi-, tri-, tetra-, penta-, and hexadentate ligands, including combinations of any two or more thereof. According to preferred embodiments thereof, the ligands of the metal complexes are selected from the group consisting of halide, pseudohalide, H_2O, NH_3, CO, hydroxide, oxalate, ethylenediamine, 2,2'-bipyridine, 1,10-phenanthroline, acetylacetonate, 2,2,2-crypt, diethylenetriamine, dimethylglyoximate, EDTA, ethylenediaminetriacetate, glycinate, triethylenetetramine, tris(2-aminoethyl)amine, and combinations of two or more thereof, more preferably from the group consisting of fluoride, chloride, bromide, cyanide, cyanate, thiocyanate, NH_3, CO, hydroxide, oxalate, ethylenediamine, acetylacetonate, diethylenetriamine, dimethylglyoximate, EDTA, ethylenediaminetriacetate, glycinate, triethylenetetramine, tris(2-aminoethyl)amine, and combinations of two or more thereof, more preferably from the group consisting of chloride, bromide, cyanide, NH_3, CO, oxalate, ethylenediamine, acetylacetonate, diethylenetriamine, EDTA, thylenediaminetriacetate, triethylenetetramine, and combinations of two or more thereof, more preferably from the group consisting of cyanide, ethylenediamine, acetylacetonate, diethylenetriamine, EDTA, ethylenediaminetriacetate, triethylenetetramine, and combinations of two or more thereof, wherein more preferably the complex ligand is cyanide, and wherein even more preferably the metal complex comprises hexacyanoferrate, preferably hexacyanoferrate(II).

With respect to the impregnation procedure employed in step (vi), any suitable impregnation means may be employed involving the use of any suitable solvent system to this effect depending on the type and amount of the one or more sources for the one or more elements selected from the group consisting of Fe, Ru, Ir, and combinations of two or more thereof. Thus, by way of example, the solvent system employed for the impregnation procedure is not particularly restricted provided that the dissolution and/or suspension of the one or more sources for the one or more elements may be achieved for the impregnation process. Thus, in the event that the one or more sources of the one or more elements is used in the form of one or more metal complexes and/or organometallic compounds which are charge neutral and/or which may be dissolved without solvation of at least part of the one or more metal compounds, any suitable solvent system may be employed to this effect wherein preferably a solvent system comprising one or more organic solvents may be used to this effect.

As regards the organic solvents which may be employed according to said particular embodiments of the present invention, these may be selected among non-polar solvents, polar aprotic solvents, and polar protic solvents, including mixtures of two or more thereof, wherein the non-polar solvents may for example be selected from the group consisting of pentane, cyclopentane, hexane, cyclohexane, benzene, toluene, 1,4-dioxane, chloroform, and diethylether. The polar aprotic solvents may be for example selected from the group consisting of dichloromethane, tetrahydrofurane, ethylacetate, acetone, dimethylformamide, acidonitrile, dimethylsulfoxide, and propylenecarbonate. Finally, as polar protic organic solvent any one or more of formic acid, N-butanol, isopropanol, N-propanol, ethanol, methanol, and acidic acid may be used to this effect. As regards embodiments of the present invention wherein the one or more sources for the one or more elements in step (vi) comprise one or more metal salts which are impregnated into the pillared silicate in their dissociated, i.e. in the solvated state, it is accordingly preferred that the solvent system used to this effect comprises a polar protic solvent which may for example be selected from the group consisting of N-propanol, ethanol, methanol, acidic acid, and water including mixtures of two or more thereof, wherein according to said embodiments of the inventive process the solvent system comprises ethanol, methanol, water, or mixtures of two or more thereof, and more preferably comprises water, wherein it is particularly preferred in said cases that water is used as the solvent system for the impregnation in step (vi) of the inventive process.

Thus, concerning the means of impregnation employed in step (vi) of the inventive process, again any suitable means may again be used to this effect such as by contacting the pillared silicate obtained in step (v) with a solvent system comprising the one or more sources of the one or more elements selected from the group consisting of Fe, Ru, Ir, and combinations of two or more thereof according to any of the particular or preferred embodiments defined in the present application. Said contacting may be performed such that an excess of the solvent system containing the one or more sources for the one or more elements is employed in excess for achieving the impregnation of the pillared silicate which is then filtered off from the solution and optionally dried and/or calcinated. According to an alternative embodiment of the present invention, however, the impregnation in step (vi) is achieved by incipient wetness such that the pillared silicate obtained in step (v) is treated with a specific amount of a solvent system comprising the one or more sources for the one or more elements allowing for complete absorption thereof into the micro- and/or mesoporous system of the pillared silicate.

As regards preferred embodiments of the inventive process wherein the one or more elements impregnated into the pillared silicate in step (vi) are employed in the form of a metal compound and in particular in the form of a metal complex and/or an organometallic compound, it is preferred that the impregnated silicate is subject to a further step for transforming the one or more metal compounds into the metal and/or into a metal oxide of the one or more elements selected from the group consisting of Fr, Ru, Ir, including alloys and/or mixed oxides of any two or more thereof. As for the degradation of the one or more swelling agents in step (v), any suitable means may be employed for degrading the counterions and/or ligands and/or organometallic moieties wherein the particular and preferred means relative to the degradation of the one or more swelling agents as defined in the present application apply accordingly with respect to the degradation of the aforementioned counterions, ligands, and/or organometallic moieties, i.e. organic moieties bound to the metal in the organometallic compounds. In particular, according to said preferred embodiments, it is particularly preferred that the impregnated pillared silicate obtained in step (vi) is subject to a degradation procedure and in particular to a calcination procedure according to any of the particular or preferred embodiments relative to the degradation of the one or more swelling agents for obtaining a pillared silicate loaded with one or more elements selected from the group consisting of Fe, Ru, Ir, and combinations of two or more thereof, wherein said one or more elements are, at least in part, present in the pillared silicate as the metal and/or as an oxide of said metal or metals, wherein in the event that two or more metals have been impregnated into the pillared silicate in step (vi), two or more of said two or more elements may be contained in the pillared silicate in the form of an alloy and/or a mixed oxide of two or more of said two or more elements.

As regards the workup of the impregnated pillared silicate obtained in step (vi), any suitable one or more steps may be conducted which according to particular and preferred embodiments include a step of calcining the impregnated pillared silicate. Thus, by way of example, the impregnated pillared silicate obtained in step (vi) may be subject to any number and/or sequence of washing and/or drying steps preferably prior to calcination thereof according to the particular and preferred embodiments of the inventive process including said step. It is, however, preferred according to the present invention that the pillared silicate obtained in step (vi) of the inventive process is simply dried without having been subject to a washing step for avoiding the loss of any portion of the one or more elements which have been impregnated into the pillared silicate in step (vi), in particular in instances wherein the washing solvent system would lead to the dissolution of at least part of the one or more sources for the one or more elements employed in step (vi).

Therefore, according to preferred embodiments of the inventive process, the production of a pillared silicate further comprises

(vii) drying the impregnated pillared silicate;

and/or

(viii) calcining the impregnated and optionally dried pillared silicate.

As regards the preferred calcination conducted in step (viii) of the inventive process, as for the calcination preferably conducted in step (v), there is no particular restriction as to the temperature which may be employed therein, wherein it is preferred that said calcination is conducted at a temperature ranging from 400 to 950 °C, preferably from 450 to 850 °C, more preferably from 500 to 750 °C, more preferably from 550 to 700 °C, and even more preferably from 600 to 650 °C.

As regards the optional workup of the impregnated pillared silicate obtained in step (vi), said optional steps may be repeated once or several times for improving the quality of the resulting material. Furthermore, depending on the desired loading of the pillared silicate, the impregnation in step (vi) may be repeated once or several times to this effect. Thus, according to preferred embodiments of the inventive process, the impregnating of the pillared silicate obtained in step (v) with Fe, Ru, Ir, or mixtures of two or more thereof in step (vi) is repeated one or more times and preferably one to three times, more preferably once or twice, and even more preferably once. According to said preferred embodiments, it is yet further preferred that in addition to repeating step (vi) one or more times, also step (vii) of drying the respectively impregnated silicate is repeated one or more times such that it is particularly preferred that steps (vi) and (vii) are repeated one or more times, preferably one to three times, more preferably once or twice and even more preferably once. According to said preferred and particularly preferred embodiments, it is further preferred that step (viii) of calcining the respectively impregnated and dried pillared silicate is equally repeated one or more times such that according to said further preferred embodiments, steps (vi) to (vii) are repeated one or more times, preferably one to three times, more preferably once or twice, and even more preferably once.

Therefore, according to preferred embodiments of the inventive process, step (vi), preferably steps (vi) and (vii), and more preferably steps (vi) to (viii) are repeated one or more times, preferably one to three times, more preferably once or twice, and even more preferably once.

After the optional workup of the impregnated pillared silicate obtained in step (vi) of the inventive process and in particular after preferred calcination thereof in step (viii) as defined according to particular and preferred embodiments of the inventive process, it is further preferred in addition to or alternative thereto that the pillared silicate is treated with a reducing agent.

Therefore, according to preferred embodiments of the present invention, the process for the production of a pillared silicate further comprises

(ix) treating the impregnated and optionally dried and/or optionally calcined pillared silicate with a reducing agent.

As regards the reducing agent which may be employed in step (ix), no particular restriction applies according to the present invention such that any suitable reducing agent may be employed provided that at least a portion of the one or more element selected from the group consisting of Fe, Ru, Ir, and combinations of two or more thereof impregnated into the pillared silicate may effectively be reduced by the use thereof. Thus, by way of example, the reducing agent used in step (ix) may comprise one or more compounds selected from the group consisting of hydrogen, hydrides, metals, sulfites, phosphites, hypophosphites, hydrazine, and combinations of two or more thereof, more preferably from the group consisting of hydrogen, $LiAlH_4$, diisobultyaluminum hydride, $NaBH_4$, Sn(II) salts, Fe(II) salts, sulfites, phosphites, hypophosphites, hydrazine, and combinations of two or more thereof, more preferably from the group consisting of hydrogen, $NaBH_4$, Sn(II) chloride, Fe(II) sulfate, hypophosphites, and combinations of two or more thereof, wherein even more preferably the reducing agent is hydrogen.

According to particularly preferred embodiments of the present invention, no calcination step (viii) is performed prior to step (ix) of treating the optionally dried pillared silicate with a reducing agent. According to said preferred embodiments, the impregnated pillared silicate obtained in step (vi) is therefore directly subject to treatment with a reducing agent, wherein preferably said treatment is achieved using a reducing agent in the gas form, wherein in particular reduction is performed at a temperature ranging anywhere from 100 to 600 °C with a gaseous reducing agent. More preferably, reduction in step (ix) is performed at a temperature ranging from150 to 550 °C according to said particularly preferred embodiments, and more preferably from 200 to 520 °C, more preferably from 250 to 500 °C, more preferably from 300 to 480 °C, more preferably from 350 to 450 °C, more preferably from 380 to 430 °C, more preferably from 390 to 410 °C. According to said particular and preferred embodiments, there is no particular restriction as to the gaseous reducing agent which may be used, provided that at least a portion of the one or more elements impregnated into the pillared silicate in step (vi) may be reduced, wherein preferably H_2 is used as the gaseous reducing agent.

According to the present invention, there is no particular preference relative to the one or more elements selected from the group consisting of Fe, Ru, Ir, and any combinations of two or more thereof which are chosen for impregnation into the pillared silicate in step (vi). According to particularly preferred embodiments of the present invention, the pillared silicate obtained in step (v) is impregnated with one or more elements including iron, wherein it is yet further preferred that only iron is impregnated into the pillared silicate in step (vi) of the inventive process.

Therefore, embodiments of the inventive process are particularly preferred, wherein in step (vi) the element is Fe.

In addition to the process for the production of a pillared silicate according to any of the particular or preferred embodiments defined in the present application, the present invention further relates to a pillared silicate which is obtainable according to the inventive process for the production of a pillared silicate including any one of the particular and preferred embodiments thereof. In particular, the present invention relates to pillared silicates which may either be obtained according to any one of the particular and preferred embodiments of the inventive process, as well as to a pillared silicate which may be obtained according to any of the aforementioned particular and preferred embodiments, but which however have been obtained according to a different process than the one defined in the present application.

Furthermore, the present invention also relates to a pillared silicate *per se* comprising an interlayer expanded layered silicate structure, wherein the BET surface area of the pillared silicate as determined according to DIN 66131 ranges from 900 to 1500 m^2/g. Although the aforementioned pillared silicate according to the present invention may be obtained according to any conceivable method, it is preferred that said pillared silicate is a pillared silicate obtainable according to the inventive process as defined in any one of the particular or preferred embodiments, and even more preferably is a pillared silicate which is obtained according to any one of said embodiments of the inventive process.

As regards the BET surface area of the pillared silicate, it has quite surprisingly been found that a pillared silicate may be provided according to the present invention which displays far higher surface areas than those which may be obtained according to the teaching of the prior art. More preferably, the BET surface area of the pillared silicate according to the present invention as determined according to DIN 66131 may range from 950 to 1,450 m^2/g, wherein more preferably, the surface area of the pillared silicate ranges from 1,000 to 1,400 m²/g, more preferably from 1,050 to 1,350 m²/g, more preferably from 1,100 to 1,300 m²/g, and even more preferably from 1,150 to 1,250 m²/g.

As regards the pillared silicate according to the present invention, which is defined by a specific surface area, it is noted that said embodiment of the present invention wherein said pillared silicate is preferably obtainable according to the inventive process does not necessarily involve either of steps (v) or (vi) for being obtained. Thus, according to said preferred embodiments of the present invention, the pillared silicate having a BET surface area as determined according to DIN 66131 ranging from 900 to 1,500 m^2/g is preferably obtainable according to a process comprising steps (i) to (iv) and more preferably comprising steps (i) to (v) of the inventive process wherein same applies with respect to particular and preferred embodiments of the individual steps (i) to (iv) and preferably steps (i) to (v) as defined in the present application relative to the corresponding steps in particular and preferred embodiments of the inventive process for the production of a pillared silicate.

Nevertheless, it is particularly preferred that, as defined in the foregoing, the pillared silicate of the present invention displaying a specific surface area as determined according to DIN 66131 ranging from 900 to 1,500 m^2/g is obtainable and even more preferably is obtained according to any of the particular or preferred embodiments of the inventive process.

Thus, according to preferred embodiments of the invention, the pillared silicate additionally contains one or more elements supported on the pillared silicate. In this respect, no particular restriction applies relative to the one or more elements which may be supported thereon, wherein it is preferred that said one or more elements comprise one or more transition metal elements, and more preferably one or more elements selected form the group consisting of Sn, Ti, Mo, Mn, Fe, Co, Cu, Zn, Zr, Ru, Pd, Ag, Pt, Au, Ir, Rh, Sm , Eu, and combinations of two or more thereof, and more preferably from the group consisting of Ti, Mo, Fe, Co, Cu, Ru, Pd, Ag, Pt, Au, Ir, Rh, and combinations of two or more thereof. According to particularly preferred embodiments of the inventive pillared silicate, the one or more elements preferably supported on the pillared silicate are selected from the group consisting of Fe, Ru, Ir, and combinations of two or more thereof, wherein even more preferably the pillared silicate further contains Fe which is supported thereon.

Therefore, embodiments of the inventive pillared silicate are preferred, wherein the pillared silicate additionally contains one or more elements supported on the pillared silicate.

As regards the one or more elements additionally contained in the inventive pillared silicate and supported thereon, there is no particular restriction according to the present invention neither regarding their number nor with respect to the amount in which the one or more elements may be contained in the pillared silicate. Thus, by way of example, the one or more elements additionally contained and supported on the pillared silicate according to any of the particular or preferred embodiments of the present invention may be present in an amount ranging anywhere from 0.1 to to 50 wt.-% based on 100 wt-% of the pillared silicate, wherein preferably the one or more elements are contained therein in an amount ranging from 0.5 to 30 wt.-%, more preferably from 1 to 25 wt.-%, more preferably from 3 to 20 wt.-%, more preferably from 5 to 16 wt.-%, more preferably from 6 to 15 wt.-%, more preferably from 7 to 14 wt.-%, and even more preferably from 8 to 13 wt.-%.

Therefore, embodiments of the inventive pillared silicate are particularly preferred, wherein the pillared silicate contains the one or more elements in an amount ranging from 0.1 to 50 wt.-% based on 100 wt-% of the pillared silicate.

According to the present invention, the pillared silicate compound may comprise any type of silicate layers, provided that said layers are suited for forming a pillared silicate structure according to particular and preferred embodiments of the present invention. As regards the term “layered silicate structure” as used in the present invention, said term generally refers to a structure comprising a regular array of silicate sheet layers which are stacked in parallel. In the present invention, the layers contained in said layered silicate structures are accordingly referred to a “silicate layers”. Thus, within the meaning of the present invention, a layered silicate structure may refer to such arrangements of silicate layers as may be found in phyllosilicates or also to regular stackings of silicate layers as may be found in layer-based zeolite structures and layered precursors of such layer-based zeolite structures. According to preferred embodiments, of the present invention, wherein the silicate layers comprise layers as may be found in a zeolite structure and/or in precursor compounds to layer-based zeolite structures, it is further preferred that said silicate layers are selected from the group consisting of zeolite-type layers. In general, such zeolite-type layers may be selected from any conceivable type of zeolite structure provided that these are suitable for forming a layered silicate structure and may form a pillared silicate according to any of the particular and preferred embodiments of the present invention. According to particularly preferred embodiments, the layered silicate structure comprises zeolite-type layers selected from the group consisting of HEU-type layers, FER-type layers, MWW-type layers, RWR-type layers, CAS-type layers, SOD-type layers, RRO- type layers, or combinations of two or more different types of these zeolite-type layers, wherein even more preferably the layered silicate structure has FER-type layers.

Therefore, embodiments of the inventive pillared silicate are further preferred, wherein the layered silicate structure comprises silicate layers selected from the group consisting of zeolite-type layers.

According to further preferred embodiments of the present invention, the layered silicate structure of the pillared silicate actually originates from one or more layered silicate compounds, preferably from a layered silicate compound which has been used in its production. In general, the term “layered silicate compound” as employed in the present invention designates any natural or synthetic layered silicate, wherein preferably said term refers to layered silicates employed as a catalyst and/or a catalyst substrate in industrial processes. Alternatively or in addition thereto, the layered silicate structure is preferably derivable from one or more silicate compounds. Regarding said layered silicate compounds from which the layered silicate structure of the pillared silicate compound preferably originates and/or may be derived from, these include one or more of any conceivable layered silicate compound provided that it is suitable for forming a pillared silicate according to any of the particular or preferred embodiments of the present invention. According to preferred embodiments of the present invention, the one or more layered silicate compounds comprise one or more zeolites. Within the meaning of the present invention, layered silicate compounds from which the layered silicate structure of the pillared silicate is preferably derived or derivable from includes derivatives of a layered silicate compound, wherein a derivative of a layered silicate compound generally refers to a layered silicate compound which has been subject to one or more physical and/or chemical modifications, preferably to one or more chemical and/or physical modification for improving its suitability to allow for a pillaring thereof according to any of the particular or preferred embodiments of the present invention.

According to particularly preferred embodiments of the present invention, said one or more layered silicate compounds comprise one or more layered silicates selected from the group consisting of MCM-22, PREFER, Nu-6(2), CDS-1, PLS-1, MCM-47, ERS-12, MCM-65, RUB-15, RUB-18, RUB-20, RUB-36, RUB-38, RUB-39, RUB-40, RUB-42, RUB-51, BLS-1, BLS-3, ZSM-52, ZSM-55, kanemite, makatite, magadiite, kenyaite, revdite, montmorillonite, and combinations of two or more thereof, wherein the one or more layered silicate compounds preferably comprise RUB-36 and/or RUB-39, and even more preferably wherein the layered silicate structure originates from RUB-36.

Therefore, embodiments of the inventive pillared silicate are yet further preferred, wherein the layered silicate structure originates from one or more layered silicate compounds and/or is derived or derivable from one or more layered silicate compounds.

Regarding the specific layered silicate compounds defined in the foregoing, RUB-18 refers to specific layered silicates of which the preparation is, for example, described in

T. Ikeda, Y. Oumi, T. Takeoka, T. Yokoyama, T. Sano, and T. Hanaoka *Microporous and Mesoporous Materials* **2008**, 110, pp. 488-500. RUB-20 refers to specific layered silicates which may be prepared as, for example, disclosed in Z. Li, B. Marler, and H. Gies *Chem. Mater.* **2008**, 20, pp. 1896-1901. RUB-51 refers to specific layered silicates of which the preparation is, for example, described in Z. Li, B. Marler, and H. Gies *Chem. Mater.* **2008**, 20, pp. 1896-1901. ZSM-52 and ZSM-55 refer to specific layered silicates which may be prepared as, for example, described in D. L. Dorset, and G. J. Kennedy *J. Phys. Chem. B.* **2004**, 108, pp. 15216-15222. Finally, RUB-38, RUB-40, and RUB-42 respectively refer to specific layered silicates as, for example, presented in the presentation of B. Marler and H. Gies at the *15th International Zeolite Conference* held in Beijing, China in August **2007**.

According to preferred embodiments of the present invention, the silicate layers of the layered silicate structure comprised in the pillared silicate compound are isomorphously substituted with one or more types of heteroatoms. In general, in said preferred embodiments, any conceivable type of heteroatom may isomorphously substitute at least a portion of the Si atoms in the silicate structure of the silicate layers, provided that the one or more types of heteroatoms are suitable for isomorphous substitution. In particular, it is preferred that the silicate layers are isomorphously substituted with one or more elements selected from the group consisting of Al, B, Fe, Ti, Sn, Ga, Ge, Zr, V, Nb, Zn, Li, Be and mixtures of two or more thereof, more preferably from the group consisting of Al, B, Fe, Ti, Sn, Zr, and mixtures of two or more thereof, more preferably from the group consisting of Al, Ti, B, and mixtures of two or more thereof, and wherein even more preferably, the silicate structure is isomorphously substituted with Al and/or Ti.

Therefore, embodiments of the inventive pillared silicate are yet further preferred, wherein the pillared silicate, and preferably the layered silicate structure of the pillared silicate, is isomorphously substituted.

In addition to the process for the production of a pillared silicate, the present invention further relates to a process for the production of one or more olefins comprising the steps of:

(1) providing a pillared silicate according to the present invention including any of the particular and preferred embodiments as defined in the present application;
(2) contacting the pillared silicate with a gas stream comprising CO and H_2.

As regards the form in which the pillared silicate may be provided in the inventive process for the production of one or more olefins, no particular restriction applies according to the present invention, provided that one or more olefins may be produced in step (2) upon contacting thereof with a gas stream comprising CO and H_2. Thus, by way of example, the pillared silicate may be provided as such or in the form of a molding or extrudate, i.e. as a shaped body which has preferably been formed with the aid of a binder.

Furthermore, no particular restriction applies relative to the mode in which the inventive process for the production of one or more olefins is conducted, such that in principle both a batch-process as well as a continuous process may be chosen. According to preferred embodiments of the present invention, however, the process for the production of one or more olefins is conducted at least in part as a continuous process.

As regards the conditions under which the pillared silicate is contacted with a gas stream comprising CO and H_2 in step (2) of the inventive process, again, no particular restriction applies in this respect provided that one or more olefins may be generated by said contacting. Thus, as regards the temperature at which said contacting is performed, said temperature may range anywhere from 100 to 700 °C, wherein preferably the temperature ranges from 150 to 500 °C, more preferably from 200 to 400 °C, and even more preferably from 250 to 350 °C. According to a particularly preferred embodiment of the inventive process the temperature at which the pillared silicate is contacted with a gas stream comprising CO and H_2 ranges from 280 to 320 °C.

Same applies accordingly with respect to the gas hourly space velocity (GHSV) of the gas stream comprising CO and H_2 which may for example range anywhere from 0.01×10^4 to 50×10^4 h^{-1}, and preferably ranges from 0.05×10^4 to 20×10^4 h^{-1}, more preferably from 0.1×10^4 to 10×10^4 h^{-1}, more preferably from 0.2×10^4 to 5×10^4 h^{-1}, more preferably from 0.5×10^4 to 2.5×10^4 h^{-1}, more preferably from 0.7×10^4 to 2.0×10^4 h^{-1}, more preferably from 0.9×10^4 to 1.8×10^4 h^{-1}, and even more preferably from 1×10^4 to 1.5×10^4 h^{-1}.

Regarding the composition of the gas stream comprising CO and H_2 which is contacted in step (2) of the inventive process, said gas stream may comprise one or more additional gases in addition to CO and H_2 such as CO_2 and/or H_2O and/or one or more inert gases including N_2. According to preferred embodiments of the present invention, however, the gas stream does not comprise any substantial amount of a further gas in addition to CO and H_2. As regards the amounts of CO and H_2 which are comprised in the gas stream for contacting with the pillared silicate, no particular restriction applies in this respect provided that at least part of the gas stream may react to one or more olefins upon contacting the pillared silicate in step (2). Thus, by way of example, the CO : H_2 molar ratio in the gas stream may range anywhere from 0.05 : 1 to 1 : 0.05, wherein preferably the molar ratio ranges from 0.1 : 1 to 1 : 0.1, more preferably from 0.3 : 1 to 1 : 0.3, more preferably from 0.6 : 1 to 1 : 0.6, more preferably from 0.8 : 1 to 1 : 0.8, and even more preferably from 0.9 : 1 to 1 : 0.9.

Finally, as regards the pressure at which the contacting in step (2) of the inventive process is performed, again no particular restriction applies in this respect provided that one or more olefins may be produced in the inventive process. Thus, the contacting in step (2) of the inventive process may range anywhere from 0.01 to 20 MPa, wherein it is preferred that said contacting is performed at a pressure ranging from 0.05 to 5 MPa, and more preferably from 0.1 to 2 MPa. According to particularly preferred embodiments of the present invention, the contacting in step (2) of the gas stream comprising CO and H_2 with the pillared silicate is performed at a pressure greater than atmospheric pressure and in particular at a pressure ranging from 0.3 to 1 MPa, more preferably from 0.4 to 0.7 MPa, wherein according to particularly preferred embodiments of the present invention, contacting in step (2) is performed at a pressure ranging from 0.45 to 0.55 MPa.

Finally, the present invention relates to the use of a pillared silicate compound as defined in the foregoing according to any of the particular and preferred embodiments described in the present application in any suitable application, wherein it is preferred that the inventive pillared silicate is employed as a molecular sieve, catalyst, catalyst component, catalyst support or binder thereof, as adsorbents, and/or for ion exchange.

The present invention is explained in more detail with reference to the examples and figures described below.

DESCRIPTION OF THE FIGURES

Figure 1	displays the X-ray diffraction pattern of the RUB-36 layered silicate used as starting material in Examples 1 and 2 as well as the RUB-36 interlayer expanded silicate and the RUB-36 pillared silicate respectively obtained according to Example 1. In the figure, the diffraction angle in °2Theta is designated as “2θ” and is plotted along the abscissa, and the diffraction intensity in arbitrary units is plotted along the ordinate. In the Figure, the diffraction patterns of RUB-36 interlayer expanded silicate is designated as “RUB-36(SW)”, whereas the diffraction patterns of RUB-36 pillared silicate is designated as “RUB-36(PS)”.
Figures 2 - 4	show both the nitrogen adsorption isotherms and the mesopore size distribution for the RUB-36 pillared silicate, the RUB-36 pillared silicate loaded with 8 wt.-% iron, and the RUB-36 pillared silicate loaded with 13 wt.-% iron respectively obtained according to Examples 1, 3 and 4. In the figures, the relative pressure “P/p_0” is plotted along the abscissa for the

nitrogen adsorption isotherm, and the pore size in nm indicated as “nm” is plotted along the abscissa for the mesopore size distribution displayed in the graph displaying the nitrogen adsorption isotherm. For the nitrogen adsorption, the values for the adsorption are indicated by the symbols “■” whereas the values obtained for the desorption are indicated by the symbols “●”, and the pore volume in ml/g is plotted in arbitrary units along the abscissa.

Figure 5 displays the X-ray diffraction patterns of RUB-36 pillared silicate obtained according to Example 1 and the RUB-36 pillared silicate loaded with iron obtained according to Example 3 with a loading of 8 wt.-% and 13 wt.-% of iron, respectively. In the figure, the diffraction angle in °2Theta is designated as “2θ(°)” and is plotted along the abscissa, and the diffraction intensity in arbitrary units is designated as “Intensity (a.u.)” and is plotted along the ordinate. In the Figure, the diffraction patterns of RUB-36 pillared silicate is designated as “RUB-36PS”, whereas the diffraction patterns of RUB-36 pillared silicate loaded with 8 wt.-% and 13 wt.-% of iron are designated as “8wt.% Fe/RUB-36PS” and “13wt.% Fe/RUB-36PS”, respectively. Furthermore, the (110)-reflection of elemental iron is indicated as a dashed vertical line and designated as “Fe (110)” for identification of the respective reflection resulting from elemental iron contained in the diffraction patterns of RUB-36 pillared silicate loaded with iron, respectively.

EXAMPLES

Example 1

Preparation of an RUB-36 interlayer expanded silicate:

The layered silicate RUB-36 layered silicate was swollen using a cetyltrimethylammonium hydroxide (CTAOH) solution at room temperature (~27°C). More specifically, 0.5 g RUB-36 was dispersed in the 35 g CTAOH solution (4%). The mixture was stirred for 48 h, then filtered and washed with deionized water, and finally dried at room temperature to obtain the RUB-36 interlayer expanded silicate.

Preparation of a pillared silicate:

1.0g of the RUB-36 interlayer expanded silicate was dehydrated under vacuum at 60°C for 2 h, then protected under Ar, and subsequently refluxed in 10 ml tetraethylorthosilicate (TEOS) for 24 h at 78°C. The mixture was filtered and dried at room temperature, thus obtaining a white powder.

1.5 g of the interlayer expanded silicate treated with TEOS was hydrolyzed at 40°C for 10h in 20 ml of an aqueous solution of NaOH having a pH = 8.0. The resulting mixture was filtered and washed with deionized water, and finally dried at room temperature.

The hydrolyzed sample was calcined under Ar (flow rate = 30 ml/min) with a heating rate of 1°C/min and kept at 450 °C for 4h. The atmosphere was then changed to air (flow rate = 30 ml/min) and the sample was calcined at 550°C for 5 h, thus affording the RUB-36 pillared silicate.

In Figure 1 the X-ray diffraction pattern of the RUB-36 layered silicate used as starting material is displayed together with the RUB-36 interlayer expanded silicate and the RUB-36 pillared silicate respectively obtained according to the present procedure. As may be taken from the shift of the highest intensity (001) peak in the X-ray diffraction patterns displayed in Figure 1, the interlayer expanded silicate is yet further expanded upon treatment and hydrolysis with TEOS for obtaining the pillared silicate.

In Figure 2, the N_2 adsorption-desorption isotherm the the RUB-36 pillared silicate is displayed, together with a plot of the mesopore size distribution as obtained by the BJH-method. The BET surface area of the RUB-36 pillared silicate was determined to 1,200 m^2/g and the total pore volume to 0.73 cm^3/g.

Example 2

Preparation of an RUB-36 interlayer expanded silicate:

The layered silicate RUB-36 was swollen by a mixture of an aqueous solution of cetyltrimethylammonium bromide (CTABr) and tetra-n-propylammonium hydroxide (TPAOH). More specifically, 0.5g RUB-36 was dispersed in the solution containing 2.5 g CTABr, 1.0 g TPAOH and 44 g water. The mixture was stirred for 48 h at RT, then filtered and washed with deionized water, and finally dried at room temperature to obtain the RUB-36 interlayer expanded silicate.

Preparation of an RUB-36 pillared silicate:

1.0 g of the RUB-36 interlayer expanded silicate was dehydrated under vacuum at 60°C for 2 h, then protected under Ar, and subsequently refluxed in 10 ml tetraethylorthosilicate (TEOS) for 24h at 78°C. The mixture was filtered and dried at room temperature, thus obtaining a white powder.

1.5g of the interlayer expanded silicate treated with TEOS was hydrolyzed at 40°C for 10 h in 20 ml of an aqueous solution of NaOH having a pH = 8.0. The resulting mixture was filtered and washed with deionized water, and finally dried at room temperature.

The hydrolyzed sample was calcined under Ar (flow rate = 30 ml/min) with a heating rate of 1°C/min and kept at 450 °C for 4 h. The atmosphere was then changed to air (flow rate = 30 ml/min) and the sample was calcined at 550°C for 5 h, thus affording the RUB-36 pillared silicate.

Example 3

Preparation of an RUB-36 pillared silicate loaded with iron:

$(NH_4)_4Fe(CN)_6$ was employed as the iron precursor to prepare an RUB-36 pillared silicate loaded with iron. More specifically, RUB-36 pillared silicate loaded with 8 wt.-% iron was prepared by impregnating 0.6 g of dried RUB-36 pillared silicate obtained from Example 1 with 1.36 g of a 20% $(NH_4)_4Fe(CN)_6$ aqueous solution via incipient wetness, following by drying of the impregnated sample at room temperature, and then at 100°C for 12 h. Finally the iron complex impregnated into the RUB-36 pillared silicate was decomposed under Ar at 630°C for 4h to afford RUB-36 pillared silicate loaded with 8 wt.-% iron.

In Figure 3, the N_2 adsorption-desorption isotherm the the RUB-36 pillared silicate loaded with 8 wt.-% iron is displayed, together with a plot of the mesopore size distribution as obtained by the BJH-method. The BET surface area of the RUB-36 pillared silicate loaded with 8 wt.-% iron was determined to 365 m^2/g and the total pore volume to 0.41 cm^3/g.

In Figure 5 the X-ray diffraction pattern of the RUB-36 pillared silicate used as starting material is displayed together with the RUB-36 pillared silicate loaded with 8 wt.-% iron obtained according to the present procedure. As may be taken from the reflection around 45° 2Theta in the X-ray diffraction pattern displayed in Figure 5 for the sample obtained according to the present procedure, iron is present as elemental iron in the RUB-36 pillared silicate structure.

Example 4

For obtaining RUB-36 pillared silicate loaded with 13 wt.-% iron, the RUB-36 pillared silicate loaded with 8 wt.-% iron obtained from Example 3 was subject to a further impregnation step wherein 0.22 g of the dried RUB-36 pillared silicate loaded with 8 wt.-

% iron was impregnated with 0.29 g of a 20% $(NH_4)_4Fe(CN)_6$ aqueous solution via incipient wetness. The impregnated sample was then decomposed under Ar at 630°C for 4h to afford RUB-36 pillared silicate loaded with 13 wt.-% iron.

In Figure 4, the N_2 adsorption-desorption isotherm the the RUB-36 pillared silicate loaded with 8 wt.-% iron is displayed, together with a plot of the mesopore size distribution as obtained by the BJH-method. The BET surface area of the RUB-36 pillared silicate loaded with 13 wt.-% iron was determined to 303 m^2/g and the total pore volume to 0.42 cm^3/g.

In Figure 5 the X-ray diffraction pattern of the RUB-36 pillared silicate loaded with 8 wt.-% iron used as starting material is displayed together with the RUB-36 pillared silicate loaded with 13 wt.-% iron obtained according to the present procedure. As may be taken from the X-ray diffraction pattern displayed in Figure 5 for the sample obtained according to the present procedure, the Fe (110)-reflection around 45° 2Theta is accordingly more intense than in the starting material, indicating that iron from the further impregnation procedure is also present as elemental iron in the RUB-36 pillared silicate structure.

Example 5

The procedure of Examples 3 was repeated, wherein after impregnation of the RUB-36 pillared silicate with $(NH_4)_4Fe(CN)_6$ aqueous solution via incipient wetness, followed by drying of the impregnated sample at room temperature and at 100°C for 12 h, the sample was not calcined. Instead, the sample was treated with hydrogen gas at 400°C for obtaining the RUB-36 pillared silicate structure loaded with 8 wt.-% of elemental iron.

Example 6

The procedure of Examples 4 was repeated using the RUB-36 pillared silicate loaded with 8 wt.-% iron obtained from Example 5, wherein after impregnation with $(NH_4)_4Fe(CN)_6$ aqueous solution via incipient wetness, followed by drying of the impregnated sample at room temperature and then at 100°C for 12 h, the sample was again not calcined. Instead, the sample was once more treated with hydrogen gas at 400°C for obtaining the RUB-36 pillared silicate structure loaded with 12 wt.-% of elemental iron.

Example 7

Catalytic testing of RUB-36 pillared silicate loaded with iron:

Respective samples of iron supported catalyst obtained from Examples 3, 4, 5, and 6 were pelleted to 40-60 mesh at 8 MPa, and then loaded into a fix-bed catalytic evaluation device. Prior to testing, the catalyst was activated under H_2 (flow rate = 30ml/min) at 400°C for 12h. After the bed temperature had cooled down to about 270°C, syngas (CO : H_2 = 1) was fed to the evaluation device. The catalytic reaction was conducted under 0.5 Mpa of syngas (CO : H_2 = 1) with a gas space hour velocity (GSHV) of 1×10^4 h^{-1}, and the temperature was elevated to 300°C to begin the active test.

After passing the reactor, all gas lines were kept at 120 °C. The effluents were analyzed using an online gas chromatograph (Agilent 7890A), which was equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID). Furthermore, four chromatography columns were installed (Porapak Q and 5 Å molecular sieves packed columns, and modified Al_2O_3 and FFAP capillary columns).

The results from catalytic testing are shown in Tables 1 and 2 below:

Table 1: Catalytic Results using Samples from Examples 3 and 4

	Example 3	**Example 4**
wt.-% Fe	8 wt.-%	13 wt.-%
CO conversion (%)	1.0	3.9
CO_2 selectivity (%)	7.6	14.9
CH selectivity (%)	86.7	78.8
CH_4	26.9	19.5
$C_2^=$-$C_4^=$	33.0	37.6
($C_2^=$-$C_4^=$)/(C_2^0-C_4^0)	2.5	3.5
C_5^+	26.6	32.1

Table 2: Catalytic Results using Samples from Examples 5 and 6

	Example 5	**Example 6**
wt.-% Fe	8 wt.-%	12 wt.-%
CO conversion (%)	6.0	11.9
CO_2 selectivity (%)	16.2	25.1
CH selectivity (%)	81.2	72.8
CH_4	21.1	16.4
$C_2^=$-$C_4^=$	35.7	38
($C_2^=$-$C_4^=$)/(C_2^0-C_4^0)	3.5	3.8
C_5^+	33.1	35.7

Thus, as may be taken from the results displayed in tables 1 and 2, a highly selective catalyst for the conversion of syngas to olefins is provided by the present invention. Furthermore, as may be taken from the results obtained for Examples 3 and 4, the catalyst acitivity may be increased by a factor of almost 4 upon increasing the loading with iron from 8 to 13 wt.-%. Yet a further increase in the catalyst activity is observed for Examples 5 and 6, wherein the preparation of the catalyst contiaining elemental iron by reaction with H_2 at 400°C (see Examples 5 and 6) as opposed to the preparation by calcination (see Examples 3 and 4). As regards said catalyst samples, an increase in activity by a factor of almost 2 is achieved by increasing the loading with elemental iron from 8 to 12 wt.-%. In all cases, an increase in the catalyst selectivity relative to the olefin product is observed when increasing the loading of the catalyst with elemental iron.

Claims

1. A process for the production of a pillared silicate comprising:
   (i) providing a layered silicate;
   (ii) interlayer expanding the layered silicate provided in step (i) comprising a step of treating the layered silicate with one or more swelling agents;
   (iii) treating the interlayer expanded silicate obtained in step (ii) with one or more hydrolyzable silicon containing compounds;
   (iv) treating the interlayer expanded compound obtained in step (iii) with an aqueous solution to obtain a pillared silicate;
   (v) removing at least a portion of the one or more swelling agents from the pillared silicate obtained in step (iv);
   (vi) impregnating the pillared silicate obtained in step (v) with one or more elements selected from the group consisting of Fe, Ru, Ir, and combinations of two or more thereof.

2. The process of claim 1, further comprising:
   (vii) drying the impregnated pillared silicate;
   and/or
   (viii) calcining the impregnated and optionally dried pillared silicate.

3. The process of claim 1 or 2, further comprising:
   (ix) treating the impregnated and optionally dried and/or optionally calcined pillared silicate with a reducing agent.

4. The process of any of claims 1 to 3, wherein the interlayer expanded silicate obtained in step (ii) is dehydrated prior to step (iii).

5. The process of any of claims 1 to 4, wherein the layered silicate provided in step (i) comprises one or more layered silicate compounds selected from the group consisting of MCM-22, PREFER, Nu-6(2), CDS-1, PLS-1, MCM-47, ERS-12, MCM-65, RUB-15, RUB-18, RUB-20, RUB-36, RUB-38, RUB-39, RUB-40, RUB-42, RUB-51, BLS-1, BLS-3, ZSM-52, ZSM-55, kanemite, makatite, magadiite, kenyaite, revdite, montmorillonite, and combinations of two or more thereof.

6. The process of any of claims 1 to 5, wherein the layered silicate provided in step (i) is isomorphously substituted.

7. The process of any of claims 1 to 6, wherein the one or more swelling agents used in step (ii) comprise one or more compounds selected from the group consisting of cationic surfactants.

8. The process of claim 7, wherein the cationic surfactant contains 1 to 4 alkyl chains having 4 C-atoms or more.

9. The process of claim 7 or 8, wherein the one or more alkyl chains having 4 C-atoms or more include one or more C_4-C_{26} alkyl chains.

10. The process of any of claims 7 to 9, wherein the cationic surfactant comprises one or more tetraalkylammonium compounds.

11. The process of any of claims 1 to 10, wherein the hydrolyzable silicon containing compound comprises one or more silicon compounds $X^1X^2SiX^3X^4$ wherein X^1, X^2, X^3, and X^4 independently from one another stand for a leaving group, wherein the leaving group X^1, X^2, X^3, and X^4 may be the same or different from one another.

12. The process of any of claims 1 to 11, wherein in step (iii) the treatment is conducted at a temperature comprised in the range of from 25°C to the refluxing temperature of the hydrolizable silicon containing compound in the mixture provided in step (iii).

13. The process of any of claims 1 to 12, wherein in step (iii) the treatment is conducted for a period of from 1 to 72 h.

14. The process of any of claims 1 to 13, wherein the aqueous solution used in step (iv) has a pH of from 5 to 10.

15. The process of any of claims 1 to 14, wherein step (v) includes a calcination step for removing at least a portion of the swelling agen.

16. The process of any of claims 1 to 15, wherein the calcination in step (viii) is conducted at a temperature ranging from 400 to 950°C.

17. The process of any of claims 1 to 16, wherein the one or more sources for the one or more elements in step (vi) comprise one or more metal compounds selected

from the group consisting of metal salts, metal complexes, organometallic compounds, and combinations of two or more thereof.

18. The process of claim 17, wherein the ligands of the metal complexes are selected from the group consisting of mono-, bi-, tri-, tetra-, penta-, and hexadentate ligands, including combinations of two or more thereof.

19. The process of any of claims 1 to 18, wherein step (vi) is repeated one or more times.

20. The process of any of claims 1 to 19, wherein the reducing agent in step (ix) comprises one or more compounds selected from the group consisting of hydrogen, hydrides, metals, sulfites, phosphites, hypophosphites, hydrazine, and combinations of two or more thereof.

21. The process of any of claims 1 to 20, wherein in step (vi) the element is Fe.

22. A pillared silicate obtainable according to the process of any one of claims 1 to 21.

23. A pillared silicate comprising an interlayer expanded layered silicate structure, wherein the BET surface area of the pillared silicate as determined according to DIN 66131 ranges from 900 to 1,500 m^2/g.

24. The pillared silicate of claim 22 or 23, wherein the BET surface area of the pillared silicate as determined according to DIN 66131 ranges from 950 to 1,450 m^2/g.

25. The pillared silicate of any of claims 22 to 24, wherein the pillared silicate additionally contains one or more elements supported on the pillared silicate, wherein the one or more elements are selected from the group consisting of Fe, Ru, Ir, and combinations of two or more thereof.

26. The pillared silicate of claim 25, wherein the pillared silicate contains the one or more elements in an amount ranging from 0.1 to 50 wt.-% based on 100 wt-% of the pillared silicate.

27. The pillared silicate of any of claims 22 to 26, wherein the layered silicate structure comprises silicate layers selected from the group consisting of zeolite-type layers.

28. The pillared silicate of any of claims 22 to 27, wherein the layered silicate structure originates from one or more layered silicate compounds and/or is derived or derivable from one or more layered silicate compounds.

29. The pillared silicate of any of claims 22 to 28, wherein the pillared silicate is isomorphously substituted.

30. A process for the production of one or more olefins comprising the steps of:
    (1) providing a pillared silicate according to any of claims 22 to 29;
    (2) contacting the pillared silicate with a gas stream comprising CO and H_2.

31. The process of claim 30, wherein the contacting in step (2) is performed at a temperature ranging from 100 to 700°C.

32. The process of claim 30 or 31, wherein the contacting in step (2) is performed at a gas hourly space velocity of the gas stream ranging from 0.01×10^4 to 50×10^4 h^{-1}.

33. The process of any of claims 30 to 32, wherein the CO : H_2 molar ratio in the gas stream ranges from 0.05 : 1 to 1 : 0.05.

34. The process of any of claims 30 to 33, wherein the contacting in step (2) is performed at a pressure ranging from 0.01 to 20 MPa.

35. Use of a pillared silicate according to any of claims 22 to 29 as a molecular sieve, catalyst, catalyst component, catalyst support or binder thereof, as absorbents, and/or for ion-exchange.

Fig. 1

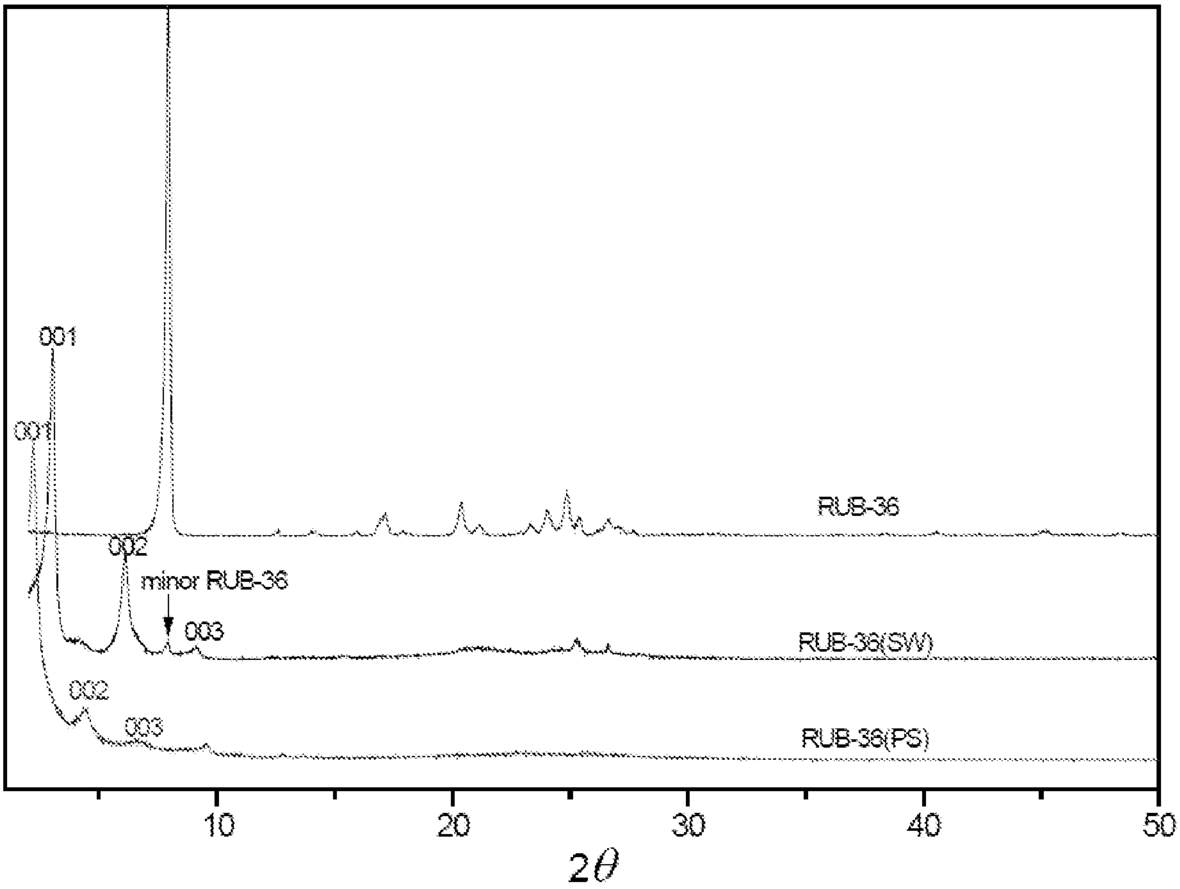
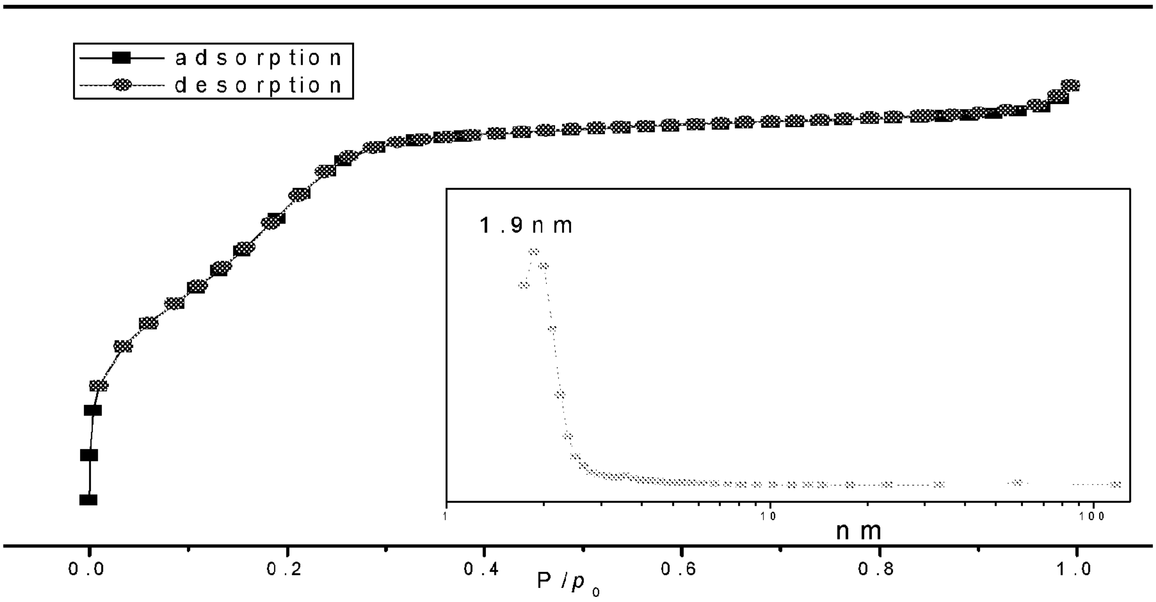

001
001
002
minor RUB-36
003
002
003
RUB-36
RUB-36(SW)
RUB-36(PS)
10
20
30
40
50
2θ

Fig. 2



p /p $_0$

Fig. 3

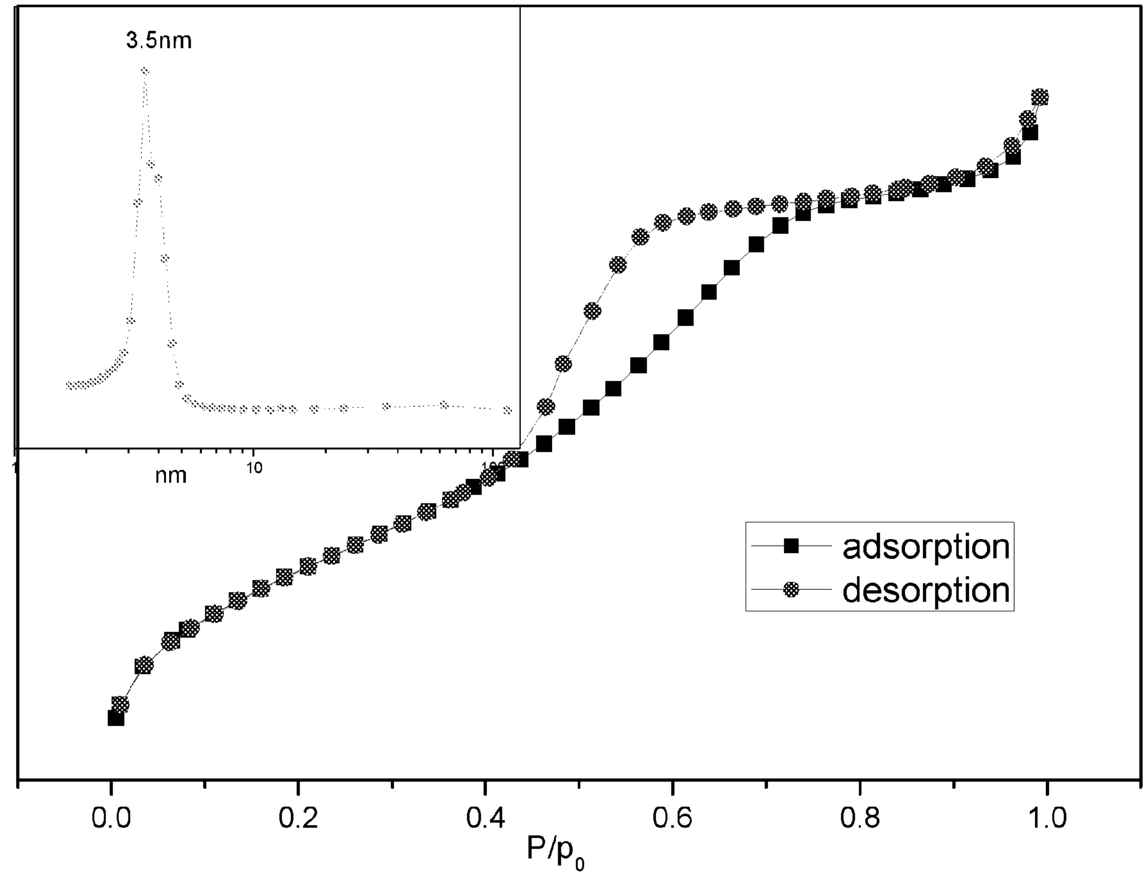


Fig. 4

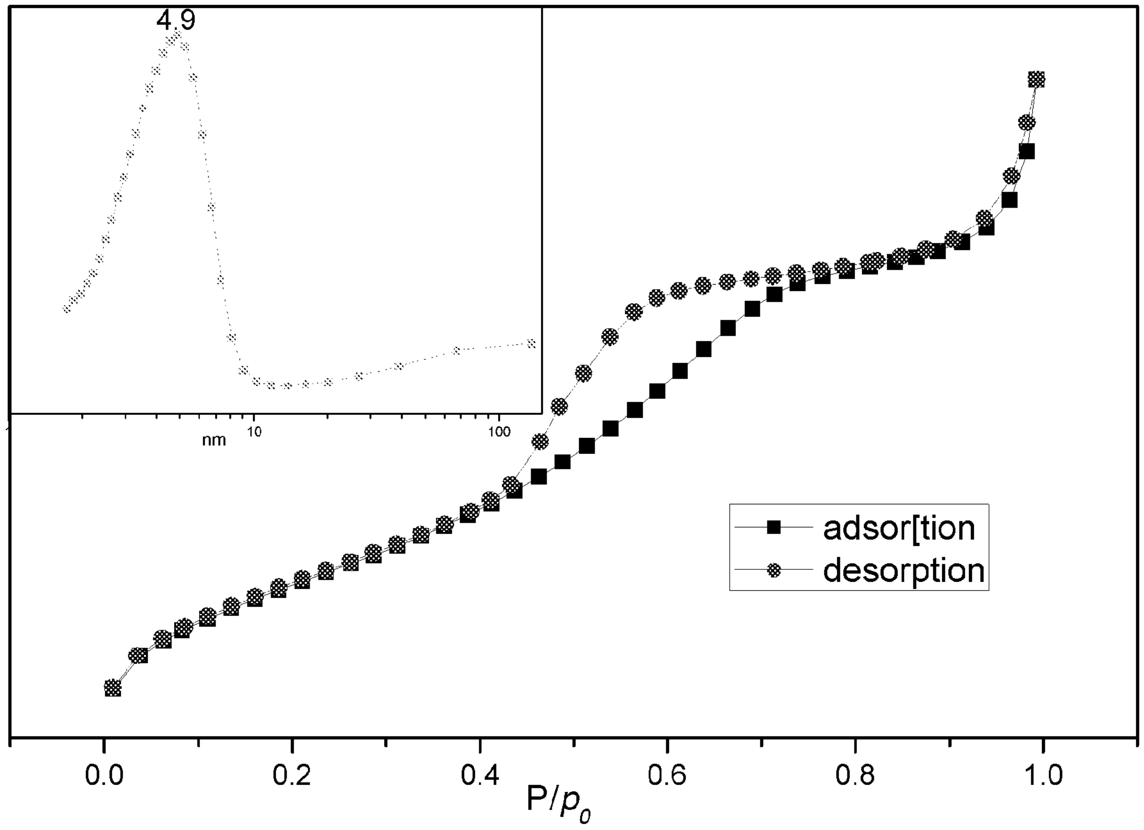
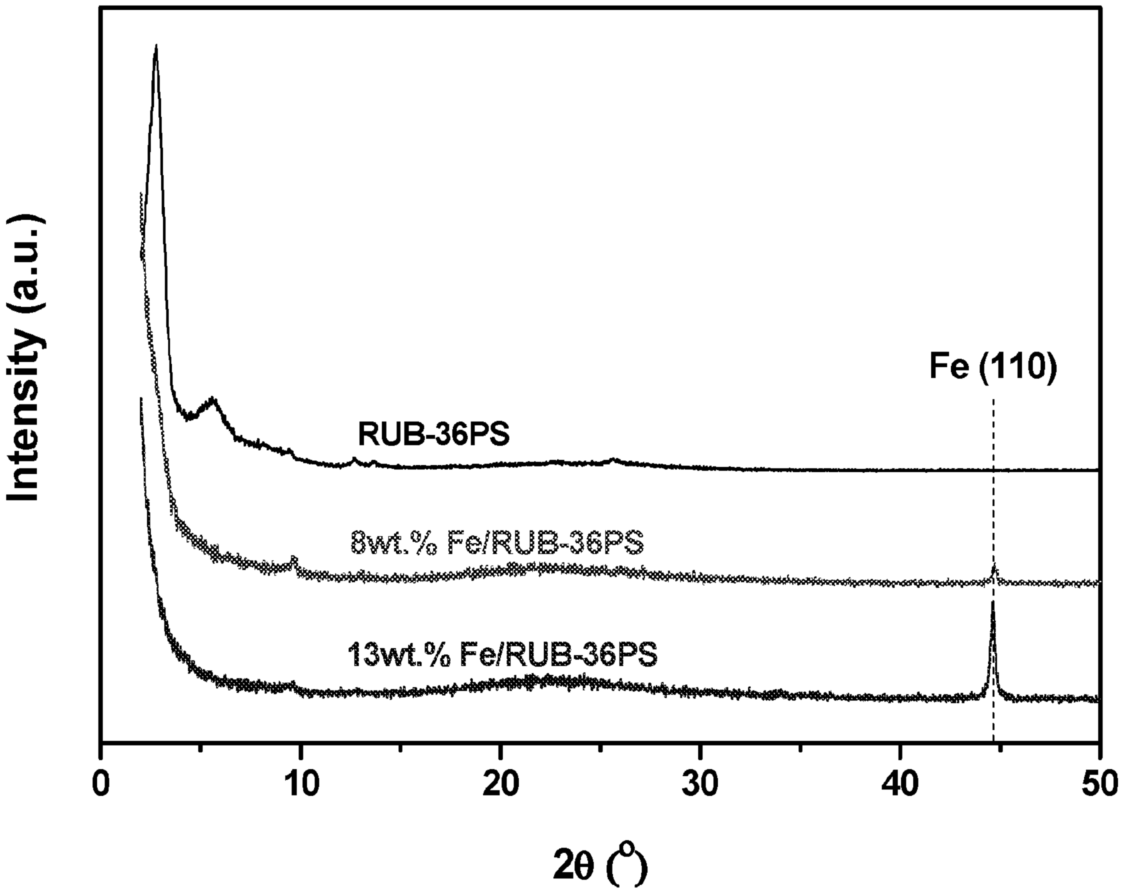


Fig. 5


Intensity (a.u.)
Fe (110)
RUB-36PS
8wt.% Fe/RUB-36PS
13wt.% Fe/RUB-36PS
0
10
20
30
40
50
2θ (°)