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(54) Title: CATALYST FOR REMOVING DETRIMENTAL HYDROCARBONS PRESENT IN EFFLUENT OR PROCESS GASES

(57) Abstract: The invention relates to a catalyst for the removal of detrimental halogenated and non-halogenated hydrocarbons in different effluent or process gases. The invention also relates to a method for the manufacture and use of such a catalyst. The catalyst of the invention comprises a porous support agent, on the surface of which there are one or several noble metals, V, and one or several 1. additives chosen from the group of Cr, Mn, Fe, Co and Ni.

Catalyst for removing detrimental hydrocarbons present in effluent or process gases

Technical background

The present invention relates to a catalyst for removing detrimental halogenated or non-halogenated hydrocarbons present in different effluent or process gases as non-detrimental compounds. The invention also relates to a method for the manufacture and use of such a catalyst.

Hydrocarbons (HC) are used as reactants, solvents, or they are generated in some processes, burning processes or under other conditions. The detrimental hydrocarbon compounds present in effluent gases are also called VOC (volatile organic compounds), which thus are gaseous in common environmental or process conditions. VOC emissions are detrimental to health and they cause local odour nuisances, because many compounds have a low odour threshold. Hydrocarbons react together with nitrogen oxides and form so-called photochemical mist by the action of the sun. Due to these reasons it is not allowed to let significant amounts of these compounds to escape from the processes together with effluent gases, and the authorities have set highest allowed concentrations or total emission amounts for the emissions.

Halogenated (chloro, bromic, fluoric and iodine HCs) hydrocarbons (H-HC) are often known to be more harmful to organisms and plants than other hydrocarbons or oxidised hydrocarbons. Also the abbreviation C-VOC is used of chlorinated hydrocarbons. Some compounds (dioxines and polycyclic aromatic compounds) are known to be carcinogenic already in low concentrations with a short exposure. These compounds are detrimental also because their biological degradation is very slow so that compounds accumulated in the body do not vanish in a natural way. Halogenated hydrocarbons also contribute to the thinning of the ozone layer surrounding the earth.

Thermal burning, absorption/adsorption methods, membranes, condensation, biological methods and catalytic burning have been used as methods for removing VOCs from gases or fluids. If hydrocarbon compounds are burned thermally in very high temperatures, it is possible to convert the major part of the detrimental compounds into water, carbon dioxide and possibly into respective hydrogen

halines. However, significant amounts of detrimental nitrogen oxides (NO_X) are generated in high temperatures.

Halogenated hydrocarbons require especially high temperatures, because they are stabile and no detrimental compounds must remain of them to the escaping gas. Residues that have to be processed are generated in the absorption and adsorption methods. E.g. activated carbon and zeolites have been used as adsorption materials, which suit well for the removal of very small amounts from effluent gases. Oxidation of detrimental compounds can be achieved also by using e.g. plasma or UV techniques. Catalytic burning methods have gained popularity, because they will produce no residue or nitrogen oxides because of the low temperature. The use of catalysts in the burning makes possible a low operation temperature (200-500 °C) so that no nitrogen oxides will be generated, but the removal efficiency of VOC and H-HC compounds is very high.

Noble metal (Pt, Pd) or base metal catalysts (Cr, Mn. Co, Ni, Fe, V) have been used for the burning of hydrocarbons and halogenated hydrocarbons in a metallic or oxidised form (Dissanayake 2006, Chemical Industries 2006 108(Metal oxides), 543). These metals are able to change their oxidation status in the reaction, which is essential in the catalytic oxidation of VOCs. Metal oxides are reduced by hydrocarbons and oxidised back by oxygen in the gas. E.g. aluminium oxide has been used as the support material for these active components. Noble metals on the surface of boric nitride also operate actively in the removal of VOC compounds (US Patent 2003/0078156).

Very good durability is required of catalysts used for the removal of halogenated hydrocarbons, because reactants and reaction products are corroding and the generating metal halogens (chlorides) deactivate catalysts. Most of the common VOC catalysts (Pt or Pd on the surface of TiO_2, Al_2O_3 or SiO_2) lose especially activeness of low temperature in the presence of H-HCs (Sinquin et al. 2000, Appl. Catal. 27(2000) 105). Most durable C_1-C-VOC catalysts are V, Cr, Mn, Fe, Co, Ni and Cu. Perovskites (e.g. $LaCoO_3$ or $LaMnO_{3+x}$) have also been used for the catalytic removal of C-VOC compounds. H-HCs have been removed by using La, Ce, Zr or Pr stabilised alumina or other oxide support material, to which a compound comprising noble metal and sulphur, such as Pt sulphide, sulphuric acid, ammonium sulphate, titanium oxide sulphate, titanium sulphate or zirconium sulphate (US 2004/0028589) has been added. It was possible to efficiently remove H-HC and other HC compounds by using a catalyst with zirconium oxide and noble metal as well as Mn, Ce and/or Co oxide together with V oxides (US 5,283,041). With a

chromium comprising catalyst it has been possible to reach a good removal efficiency of H-HC compounds (US 5,635,438, 1994). It was essential to calcine the catalyst within the temperature range of 725-1100 °C. Cr-Cu/ZSM-5 catalysts have also been used for removing chlorinated hydrocarbons (J. Hazardous Mat. B129(2006 39). C-VOC catalysts have been stabilised by pre-processing them with halide compounds (US 2001/0016555). A method has also been developed for the removal of HC and H-HC compounds, in which non-halogen compounds react in a first catalyst in a support material of low acidity and halogenated hydrocarbons in a second catalyst in a support material of high acidity (US 5,643,545, 1995). Even though development work has been done, the temperature of the catalyst has to be usually raised in H-HC subjects during use in order to be able to retain the desired level of conversion. Raising the temperature will again lead to an increase in the consumption of energy and thermal deactivation.

General description of the invention

There has now been invented a catalyst suitable for the removal of halogenated and non-halogenated hydrocarbons in effluent and process gases.

To achieve this object the invention is characterised in what is disclosed in the independent patent claims. The other patent claims show some advantageous embodiments of the invention.

The invention is based on that a fluid mixture comprising hydrocarbons is directed to a catalyst according to the invention, in which halogenated and non-halogenated hydrocarbons react as non-detrimental or less detrimental compounds.

The catalyst of the invention comprises a porous support material, on the surface of which there are:

- one or several noble metals;
- V; and
- one or several 1. additives, which have been chosen from the group comprising Cr, Mn, Fe, Co and Ni.

According to an object of the invention the support material is aluminium, silicon, titanium or zirconium oxide or zeolite, or a mixture of these.

According to an object of the invention the noble metal on the surface of the porous support material is Pt, Pd, Rh, Ru, Ir and/or Hg.

According to an object of the invention the amount of the support material is 10 – 600 g/dm$^3_{\text{catalyst structure}}$.

According to an object of the invention the total concentration of noble metals is 0.1 – 20%, preferably 0.5 – 3% in the support material.

According to an object of the invention the support material has 0.2 – 20%, preferably 1 – 5% of vanadium.

According to an object of the invention the total concentration of the 1. additive in the support material is 0.02 – 20%, preferably 0.1 – 2%.

According to an object of the invention the support material has 0.02 – 10%, preferably 0.1 – 1% of chromium as the 1. additive.

According to an object of the invention the support material also has one or several 2. additives, which have been chosen from the group of W, Mo, Nb and Hf.

According to an object of the invention the total concentration of the 2. additive is 0.02 – 50%, preferably 1 – 35%.

An embodiment of the invention is a composition, which has no vanadium but a second additive, preferably tungsten, and optionally noble metal and/or 1. additive (preferably Cr and/or Fe). The amount of W in the support material is preferably 5 – 25%, as oxide approximately 6 – 32%. The support material preferably comprises TiO_2. Excluding the vanadium is of advantage especially e.g. in the manufacture and also the use of the catalyst.

According to an object of the invention the catalyst structure is a honeycombed structure or mixing structure made of metal, ceramics, the catalyst material itself or a mixture of these and consisting of straight or tortuous flow channels, such as preferably a metallic structure or mixing structure consisting of straight or tortuous flow channels.

According to an object of the invention the catalyst has been added to a catalyst structure, in which channels have been arranged between the walls, the hydraulic diameter of the channels or the average distance of the walls from each other is 0.1 – 20mm, preferably 0.5 – 2mm.

According to an object of the invention noble metal/noble metals are added to the support material before the adding of V, and the 1. additive/additives are added to the support material after the adding of V.

According to an object of the invention the catalyst structure is a honeycombed structure or mixing structure made of metal, ceramics, the catalyst material itself or a mixture of these and consisting of straight or tortuous flow channels, preferably a metallic structure or mixing structure consisting of straight or tortuous flow channels.

The catalyst and method of the invention can be constructed in different ways in accordance with the object and objectives. The system can have one or several catalysts according to the invention or a combination of these. The catalyst of the invention can also be combined with one or several conventional or known VOC catalysts. In addition, the system can have one or several heat exchangers, with which it is possible to recover the reaction heat and to circulate it in the reactor, for example, by using a reverse flow reactor.

According to an object of the invention the catalyst is used in a unidirectional or reverse flow reactor.

According to an object of the invention more than one heat exchanger structures are used with the catalyst.

According to an object of the invention more than one heat exchanger structures and reverse flow reactors are used with the catalyst.

According to an object of the invention other types of catalysts are used with the catalyst, for example for catalysing the oxidation of hydrocarbons.

According to an object of the invention one or several catalysts are used with the catalyst, comprising at most 0.5% of vanadium and/or at most 0.5% of the 1. and 2. additive of the invention.

According to an object of the invention water, vapour, air or some other reactant comprising oxygen is fed to the reactor.

According to an object of the invention it is connected to be used with other removal methods, such as thermal, adsorption or absorption methods in the same or separate units. For example, the forming HCl or other halide compounds can be removed by using absorption methods, such as washers.

According to an object of the invention the catalyst is used for cleaning effluent gases comprising sulphur or nitrogen compounds and/or hydrocarbon compounds.

In a reverse flow reactor the system can be such that there are heat exchangers on both sides of the catalysts of the invention. The reverse flow reactor can be used for utilising reaction heat, and the reactor operates without additional heating with a relatively small amount of emissions, from the reaction of which reaction heat is generated more than the loss of energy. Conventional honeycombed heat exchanger structures (e.g. pipe or plate heat exchangers) are used in the heat exchangers, which last in the conditions of use. Some conventional heat transfer mediums (air, water, and other fluids/gases) can be used in the heat exchangers, which can be circulated between two different reactor parts. The heat transfer medium flows in a different channel system from the fluid to be processed. Additional heat can be imported to the heat exchangers or heat can be exported (cooling). In the heat exchangers, fluids can be in different channels in relation to each other in a cross, forward or counter current. Especially honeycombed structures can be made of metal foil, and the channel form consists of straight and cockled foil/plate or two cockled foil/plate structures. Also a combination of one or several reverse flow reactors and normal unidirectional pipe reactors can be used in the method so that one unit can be arranged after the reverse flow reactor. By using a combination of several reverse flow reactors it is possible to maintain different temperatures in different reactors and thus to optimise the operating windows and energy balances of the system. A combination of several reactors, whose modes of operation or conditions deviate from each other, can be used also in subjects where it is desired, for example, to remove also hydrocarbons and their derivatives simultaneously with halogenated hydrocarbons. Additional heat can be imported by electric or burner heating or fuel supply. An H-VOC catalyst also functions as an effective burning catalyst, with which the temperature of the system can be raised if a small amount of burning fuel is fed to the fluid. One unit or several units can be heated or cooled externally. Also other intermediate agents (compounds comprising oxygen or reducing compounds) or auxiliary energy (e.g. plasma for oxidation) can be used for promoting the reactions. The outcoming fluid can be led to some other cleaning unit, for example an adsorption or absorption unit, with which e.g. generated light halogen compounds (nitrogen halides) can be removed.

The catalyst according to the invention can be used in a method, in which a reactant (oxygen, air) is also fed to a pipeline e.g. in situations when necessary conditions cannot be otherwise created. Oxygen can be fed to effluent gases to mix-

tures comprising a too small amount of oxygen to remove hydrocarbon compounds. The catalyst can also be used in objects comprising a low amount of oxygen so that it is also possible to use the catalyst first for a fluid comprising too little oxygen and then for a fluid comprising an excessive amount of oxygen. The mixture is converted between the catalyst units to comprise an excessive amount of oxygen by feeding to it additional air or oxygen.

Fields of application for the invention are effluent gas applications in objects in which the mixture comprises halogenated hydrocarbons and (excessively) oxygen. The fluid can thus also be liquid-based or a mixture of liquids and gases. Catalysts according to the invention can also be used for cleaning hydrocarbon compounds comprising nitrogen, sulphur or oxygen. Sulphur and nitrogen compounds can also be other than hydrocarbon derivatives such as SO_x, H_2S, COS, NO_x, NH_3, HCN or other respective compounds. In the cleaning of effluent gases generated in the burning of sulphur-comprising fuels (e.g. diesel, coal, bio fuels) the catalyst of the invention can be used to withstand sulphur poisoning and to prevent the formation of sulphates, which adds the number of measurable particulate matter (PM). Such objects are, for example, moving vehicles and means of transportation (cars, trains, and ships) or stationary power plants or equipment. In these objects it is possible to exclude the 1. and/or 2. promoter and/or vanadium from the composition. In these objects also the noble metal charge has to be kept generally moderate (approximately 0.35 – 1.1 g/L Pt) so that too many sulphates would not be formed. Moderate Pt charges can thus be used with the additives of the invention, which are needed to guarantee a long-lasting CO and HC operation. With conventional oxidation catalysts the Pt charge has to be even below 0.04 g/L in order to avoid detrimental amounts of forming sulphates.

The catalyst compositions of the invention have been coated by spraying a coating slurry separately onto a smooth and cockled open metal foil or surface. After the coating the catalysts have been dried and calcined. Alternatively the catalyst coatings have been coated by dipping or immersing a finished, usually honeycombed metallic or ceramic catalyst structure in catalyst slurry. Also a combination of these manufacturing methods can have been used in the manufacture.

Active metals and promoters have already been added to the slurry or they have been absorbed into a coated catalyst. The coating and active components can also be added by different methods from gaseous or solid starting materials.

The catalyst coating of the invention can be pre- or post-coated to normal ceramic or metallic cells or structures, in which the aperture form (e.g. square, triangle), aperture density (10 – 2000 cpsi, apertures/square inch ~ 1 – 200 apertures/cm^2) or wall thickness (10 – 2000 µm) can vary within a large range, depending on the object of use. When the effluent gas comprises large amounts of particles or impurities, very large channel sizes can be used in the catalyst (< 100 cpsi). In objects with very little particles very small channel sizes (e.g. > 500 cpsi) can be used in the cell. A typical aperture number is between 300 – 600 cpsi). These variable values can vary also in the same cell or in subsequent cells so that benefits will be gained e.g. because of efficient mixing, low pressure loss or mechanical strength. Catalyst structures can be realised by using pellet-type, extruded or powdery catalysts.

The cell to be coated can also form a sort of a static mixing structure, either with mixing zones (e.g. bends, flow barriers or restrictions) in separate channels, or the structure has been formed by inserting cockled undulated foils or plates superimposed so that the direction of the wave crest deviates from the incoming direction of the gas and that the wave crests of the superimposed plates are divergent. In a common metal cell the wave crests of the cockled foil are parallel in relation to each other and to the main flow direction. The mixing efficiency can be adjusted by varying the angle between the wave crest and the main flow direction, which is usually 10 - 45°, preferably 10 - 20°. By using a small angle it is possible to make the crests to bear, but the counter pressure will not rise too high. In static mixers used purely for mixing the angle can be approximately 45° and the channel size can be big (cockle height > 10 mm) so that the flow in the channel can be made very turbulent. However, an optimum for the catalyst structure is a structure, in which the channel size is small (cockle height approximately 1mm) so that there is a lot of geometric surface for the catalyst coating. The angle in the catalyst structure has to be small so that the counter pressure can remain low. The mixing structure can also be produced by folding the cockled foil superimposed alternately back-and-forth so that the wave crests of the cockle bear against each other, and a mixing structure is formed. With the mixing structure, mixing of the flow in the radial direction of the pipe can be achieved, and it has no actual separate channels. The mixing structure can also achieve for the particles collecting efficiencies that are higher than the normal cell structure. The shape of the catalysts and flow channels can be round, elliptical, square, angular, or a combination of these. Insulation material and/or heat transfer structures/equipment may be arranged around or inside the reactor. The structure to be coated can be or instead

of the metal foil it is also possible to use partly or entirely metal mesh, sintered porous metal, fibre, or a particle catch.

The catalyst of the invention can also be coated onto two or several catalyst structures sequential or parallel in the flow direction. Catalyst structures of different or same sizes can be located in the same catalyst converter or they can be arranged in separate converters so that there is a necessary amount of pipes between them. The catalysts' inventive compositions, noble metal charges (e.g. Pt), aperture numbers (geometrical areas) or structures can be similar to or different from each other.

Detailed description of the invention

Some embodiments of the invention will be explained next in more detail, referring to the enclosed tables, in which

Table 1 illustrates cell catalysts used in activeness tests,

Table 2 illustrates gas compositions used in a laboratory simulation,

Table 3 illustrates activeness test results.

Manufacture of catalysts described in the examples:

Slurry was manufactured of catalyst raw materials, to which active agents and binding agents were added, the purpose of which was to ensure adhesion and cohesion on the surface of the support structure. Al and Ti sols were used as binding agent. A smooth and cockled metal foil with a thickness of 50 µm was coated with the prepared slurry; the samples were dried in approximately 110 °C and calcined for 4 hours in 550 °C. A desired amount of Pr, Pd, Rh, Cr and V was absorbed to the catalyst using Pt-ammine-carbonate, Pd nitrate, Rh nitrate, Cr nitrate or ammonium vanadate solutions as initial material. The used absorption methods were based on the filling of pores with the desired solution or on the chemisoprtion-type adhesion of the active component onto the surface of the support agent. With these methods the active components were dispersed as small particles to the surface of the catalyst. After the absorption the catalyst was dried in approximately 80 – 300 °C and calcined in air. A honeycombed sample was obtained by wrapping together a smooth and a cockled coated foil. The specific area of the active support agent with different samples was approximately 50 – 300 m^2/g after the

preparation. The amount of support agent on the surface of metal foil was approximately 40 – 60 m^2/g or 150 – 230 g/L in the cell.

The catalysts' activeness was tested in laboratory conditions, simulating effluent gases, which comprise chlorinated hydrocarbons, water and air. There is usually not very much water present in natural effluent gases, but it was fed with the objective of promoting catalytic reactions. The composition of the laboratory reactor's feed was adjusted by computer-controlled mass flow regulators, and the composition was analysed by continuous FTIR analysers, with which it was possible to separate different hydrocarbons and reaction products from each other. In some tests the feed gases comprised bromated hydrocarbons or dimethylformamide (DMF). The conditions in the measurement of activeness by laboratory equipment were the following.

Example 1

The oxidation of DCM and PCE was tested in a laboratory reactor test in two separate tests, in which these compounds were fed individually to the reactor together with oxygen and water (Tables 2-3). By adding both V and C to the catalyst it was possible to increase activeness especially in relation to PCE (tests 1-6). Without active base metal elements it was not possible to achieve the desired activeness even by increasing the noble metal charge (test 12). Increasing the charge to 250 g/cft PtPd (1:4) did not much improve the activity. A higher charge can have a positive effect in longer use. With Pt/Al_2O_3+0.5Cr+3.2V catalyst the increase of the Pt charge from 50 to 90 g/cft promoted the oxidation of PCE (tests 6 an 11).

Example 2

Effluent gases do not often comprise large concentrations of water. As hydrocarbons become oxidised, fair amounts of water are naturally formed to the mixture. It was noted in the tests that water added to the gas to be purified began to improve the activity (0 → 3% water, tests 3, 6 and 8, 9). By reducing the space velocity and by increasing the amount of water with a catalyst comprising Pt and PtPd, the ignition temperatures decreased (test 8-9, 13-16). Thus, when using the catalyst of the invention it is possible to add water to the mixture to be purified, and the size of the catalyst is planned in accordance with the desired operating temperature and conversion objective.

Example 3

A catalyst according to the invention comprising Cr and V is more active, if it also includes noble metals (test 19 vs. test 6). $PtRh/Al_2O_3$ was very active to DCM, but very weak to PCE. By adding Cr and V, the ignition temperature for PCE could be decreased by 81 °C (tests 17 and 18). Because Pt and PtRh catalysts were active in the removal of DCM, it is possible to use a catalyst combination in which at least one cell comprises only noble metals and a second cell comprises also V and Cr or similar elements according to the invention.

Example 4

Without noble metals TiO_2+Cr+V and TiO_2+Cr+V+W catalysts functioned well in relation to PCE, but the activeness for DCM was poor (tests 20 and 21). By adding Pt to these catalysts, it was possible to decrease the ignition temperature for DCM (tests 22 and 23). An especially low ignition temperature for PCE (330 °C) could be reached with $50Pt/Al_2O_3$+Cr+V+W catalyst, which temperature is approximately 200 °C lower than with the known C-VOC catalysts. When using a catalyst comprising W, the ignition temperature for DCM was 400 °C so it can be deducted that good DCM and PCE removal activities can be achieved by combining it to successive cells with, for example, Pt/Al_2O_3, $PtRh/Al_2O_3$ or a similar oxidation catalyst.

Example 5

A catalyst of the invention ($50Pt/Al_2O_3$-0.5Cr-3.2V) removed efficiently dimethylformamide (DMF) when the T_{50} value was 227 °C (space velocity 28,000 h^{-3} and 0.47 ml/h DMF, no water). With the catalyst of the invention it is thus possible to efficiently remove also nitrogen-comprising hydrocarbon derivatives. The catalyst can also be used for the catalytic removal of hydrocarbon compounds or hydrocarbons comprising other functional groups (comprising oxygen, sulphur and nitrogen, different C-H bonds) from effluent gases.

Example 6

Catalysts of the invention were also prepared in versions, which comprised no V. The catalysts had a high WO_3 concentration (26%), and especially the DCM conversions were low. With the catalyst 40 g/cft Pt/TiO2+26WO_3, T_{50} for DCM was 299 °C. When still 0.5% Cr or 3% Fe was added to the same base, the ignition temperatures for DCM were 255 and 276 °C. In these samples the aperture number was 600 cpsi, when there was slightly more support agent than in the cells of 500 cpsi, but nevertheless, the difference in relation to the support agent amount was not significant. The Pt charge was only 40 g/cft (1.41 g/L) so that low ignition

temperatures could be reached in the catalysts of the example without vanadine, with a lower amount of expensive Pt and even without Cr. However, a distinct improvement could be achieved with Cr to PCE conversions. In the tests 20-24 it is also seen how TiO_2 has an advantageous effect as the main component for the support agent compared, for example, with Al_2O_3.

Example 7

Catalysts according to the invention were used in the purification of diesel exhaust gas (simulation mixture: 1500 ppm CO, 80 ppm propene, 15 ppm toluene, 15 ppm decane, 14% oxygen, 6% CO_2, 25 ppm SO_2, and the balance nitrogen (space velocity 30,000). The samples were aged hydrothermally in 700 °C for 20 hours and sulphurated for 1 hour in 420 °C in exhaust gas contaning 50 ppm SO_2. After sulphurisation the catalyst no longer aggregated sulphur. With the sulphurisation it was ensured that the catalyst does not absorb sulphur in the ignition run, but the test conditions correspond to the normal situation with a catalyst that has been in use for a slightly longer period. An ignition run was performed with a sulphurised sample using the mixture mentioned above. The formation of sulphate can be examined on the basis of the SO_2 conversion. SO_2 becomes oxidised to SO_3 especially in an oxidation catalyst comprising Pt, which further reacts into sulphates in the presence of water. When in common oxidation catalysts the SO_2 conversion is easily over 60 – 70% after the ignition temperature, with a sample comprising V and W ($20Pt/TiO_2+16SiO_2+1.9V0+13WO_3$) the maximum level of 27% remained at 250 °C and on average below 5% between 100 – 450 °C in an ignition test. At the same time, the CO ignition temperature was 160 °C and the HC ignition temperature 228 °C so that sulphurisation and the presence of sulphur in exhaust gas does not prevent desired reactions. A relatively low Pt charge is also essential to keep the oxidation of SO_2 and the formation of sulphates low. Such a catalyst is suitable for the purification of exhaust gases in motors using fuels with a high sulphur concentration (CO, HC, particles). When the formation of sulphates has been minimised, the mass of particles can be reduced by such catalysts, because the volatile part of particles becomes partly oxidised in the catalyst. In these subjects it is possible to use the above described catalyst or catalysts, which do not comprise at all V, but the 1. or 2. additive and one or several noble metals.

The catalyst $70Pt/TiO_2+13SiO_2+27Al_2O_2+3WO_3$ was sulphurised and aged in the same way as the catalyst mentioned above, but it was tested in a different mixture (500 ppm CO, 200 ppm NO, 160 ppm propene, 12% oxygen, 6% water and 6% CO_2, 25 ppm SO_2 and the balance nitrogen (space velocity 50,000 h^{-1}). The cata-

lyst resisted well the influence of sulphur, and the CO ignition temperature was 155 °C and the HC ignition temperature 186 °C (T_{50}).

Patent claims

1. Catalyst for the purification of halogenated and non-halogenated hydrocarbons and/or their derivatives in effluent and process gases, **characterised** in that the catalyst comprises a porous support agent, on the surface of which there are:
- one or several noble metals,
- V, and
- one or several 1. additives, which have been chosen from the group of Cr, Mn, Fe, C and Ni.

2. Catalyst according to claim 1, **characterised** in that the support agent is aluminium, silicon, titanium or zirconium oxide or zeolite or a mixture of these.

3. Catalyst according to claim 1 or 2, **characterised** in that the noble metal on the surface of the porous support agent is Pt, Pd, Rh, Ru, Ir and/or Hg.

4. Catalyst according to one of the preceding claims, **characterised** in that the amount of support agent is 10 – 600 $g/dm^3_{catalyst\ structure}$.

5. Catalyst according to one of the preceding claims, **characterised** in that the total concentration of noble metals is 0.1 – 20%, preferably 0.5 – 3% in the support agent.

6. Catalyst according to one of the preceding claims, **characterised** in that the support agent has vanadium in the amount of 0.2- 20%, preferably 1 – 5%.

7. Catalyst according to one of the preceding claims, **characterised** in that the total concentration of the 1. additive in the support agent is 0.02 – 20%, preferably 0.1 – 2%.

8. Catalyst according to one of the preceding claims, **characterised** in that support agent has as the 1. additive 0.02 -10%, preferably 0.1 – 1% of chromium.

9. Catalyst according to one of the preceding claims, **characterised** in that the support agent further has one or several 2. additives, which have been chosen from the group of W, Mo, Nb and Hf.

10. Catalyst according to claim 9, **characterised** in that the total concentration of the 2. additive is 0.02 - 50%, preferably 1 – 35%.

11. Catalyst according to one of the preceding claims, **characterised** in that the catalyst structure is a honeycombed structure or mixing structure consisting of straight or curved flow channels and made of metal, ceramics, the catalyst material itself or a mixture of these, such as preferably a metallic structure or mixing structure consisting of straight or curved flow channels.

12. Catalyst according to one of the preceding claims, **characterised** in that the catalyst has been added to the catalyst structure, in which there are channels between the walls, the hydraulic diameter of the channels or the average distance of the walls from each other being 0.1 – 20mm, preferably 0.5 – 2mm.

13. Method for the manufacture of a catalyst for the processing of halogenated and non-halogenated hydrocarbons and/or their derivatives in effluent and process gases, **characterised** in that a porous support agent is arranged to the catalyst, to the surface of which is added:
- one or several noble metals,
- V, and
- one or several 1. additives, which have been chosen from the group of Cr, Mn, Fe, Cr and Ni.

14. Catalyst according to claim 13, **characterised** in that the support agent is aluminium, silicon, titanium or zirconium oxide or zeolites or a mixture of these.

15. Catalyst according to claim 13 or 14, **characterised** in that the noble metal on the surface of the porous support agent is Pt, Pd, Rh, Ru, Ir amd/or Hg.

16. Catalyst according to claim 13 – 15, **characterised** in that further one or several 2. additives are added to the support agent, which are chosen from the group of W, Mo, Nb and Hf..

17. Method according to claim 13 – 16, **characterised** in that the noble metal/metals are added to the support agent before the adding of V and the 1. additive/additives are added to the support agent after the adding of V.

18. Method according to claim 14 – 17, **characterised** in that vanadium is added to the catalyst from a solution comprising oxalic acid.

19. Method for the purification of halogenated and non-halogenated hydrocarbons and/or their derivatives in effluent and process gases, **characterised** in that

effluent and process gases are processed with the catalyst according to claims 1 – 12.

20. Method according to claim 19, **characterised** in that the catalyst is used in a unidirectional or reverse flow reactor.

21. Method according to claim 19 – 20, **characterised** in that more than one heat exchanger structures are used with the catalyst.

22. Method according to claim 19 – 21, **characterised** in that more than one heat exchanger structure and reverse flow reactors are used with the catalyst.

23. Method according to 19 – 22, **characterised** in that other types of catalysts are used with the catalyst, preferably for catalysing the oxidation of hydrocarbons.

24. Method according to claim 19 – 23, **characterised** in that one or several catalysts comprising at most 0.5% of vanadium and/or at most 0.5% of the 1. and 2. additive of the invention are used with the catalyst.

25. Method according to claim 19 – 24, **characterised** in that water, vapour, air or other oxygen comprising reactant is fed to the effluent gas in the reactor.

26. Method according to claim 19 – 25, **characterised** in that it is connected to be used together with other removal methods, such as thermal, adsorption or absorption methods in the same or separate units.

27. Method according to claim 19 – 26, **characterised** in that effluent gases comprising sulphur or nitrogen compounds and/or hydrocarbon compounds are purified with the catalyst.

28. Catalyst for the purification of halogenated and non-halogenated hydrocarbons and/or their derivatives in effluent and process gases, **characterised** in that the catalyst comprises a porous support agent, on the surface of which there are:
- one or several second additives, which are chosen from the group of W, Mo, Nb and Hf.

29. Catalyst according to claim 28, **characterised** in that the support agent further includes
- one or several noble metals and/or
- one or several 1. additives, which are chosen from the group of Cr, Mn, Fe, Cp and Ni.

30. Catalyst according to claim 28 or 29, **characterised** in that the concentration of the 2. additive in the support agent is 0.02 – 50%, preferably 1 – 35%.

Table 1. Cell catalysts used in activeness tests

No	Catalyst code	Support agent g/L	Active metal g/L (Pt, Pd, Rh)	Apertures cpsi
N1	50PtPd(2:1)/Al_2O_3	156	1.76	500
N2	50Pt/Al_2O_3+0.5Cr	156	1.76	500
N3	50Pt/Al_2O_3+0.5Cr+3.2V	156	1.76	500
N4	50Pt/Al_2O_3+0.5Cr+3.2V	222	1.76	500
N5	100PtPd(1:4)/Al_2O_3+0.5Cr+3.2V	202	3.53	500
N6	250PtPd(1:4)/Al_2O_3+0.5Cr+3.2V	155	8.82	300
N7	90Pt/Al_2O_3+0.5Cr+3.2V	155	3.18	300
N8	250PtPd(1:4)/Al_2O_3	155	8.82	300
N9	50Pt/Al_2O_3+0.5Cr+3.2V	156	1.76	500
N10	50PtRh(5:1)/Al_2O_3	156	1.76	500
N11	50Pt/Al_2O_3+3.2V	156	1.76	500
N12	50Pt/Al_2O_3+0.5Cr+3.2V	156	1.76	500
N13	50Pt/Al_2O_3	156	1.76	500
N14	50PtRh(5:1)/Al_2O_3+0.5Cr+3.2V	156	1.76	500
N15	Al_2O_3+0.5Cr+3.2V	156	-	500
N16	TiO_2+0.5Cr+3.2V	156	-	500
N17	TiO_2+0.5Cr+3.2V+10WO_3	156	-	500
N18	50Pt/TiO_2+0.5Cr+3.2V	156	1.76	500
N19	50Pt/TiO_2+0.5Cr+3.2V+10WO_3	156	1.76	500
N20	40Pt/TiO_2+26WO_3	175	1.41	600
N21	40Pt/TiO_2+26WO_3+0.5Cr	175	1.41	600
N22	40Pt/TiO_2+26WO_3+3Fe	175	1.41	600
N23	TiO_2+26WO_3	172	-	600
N24	TiO_2+0.5Cr+26WO_3	175	-	600
N25	20Pt/TiO_2+16SiO_2+1.9V+13WO_3	155	0.71	300
N26	70Pt/TiO_2+13SiO_2+27Al_2O_3+3WO_3	175	2.47	400

Cpsi=cells per square inch. Geometrical area: 600 cpsi ~ 4.4 m^2/L, 500 cpsi ~ 3.9 m^2/L, 400 cpsi ~ 3.5 m^2/L, 300 cpsi ~ 3.1 m^2/L. In the catalyst code, active metal as g/cft value and others in % of the compound in question in the support agent.

Fig. 1

Table 2. Gas concentrations used in laboratory simulation

Compound	Mixture 1	Mixture 2
DCM, ppm	500	-
PCE, ppm	-	500
H_2O, %	0-3	0-3
O_2, %	~ 21.4	~ 21.4
N_2	the balance	the balance
Space velocity, h^{-1}	14,000 or 28,000	

DCM = dichloromethylene, PCE = perchloroethylene
Space velocity (SV) = exhaust gas flow/catalyst cell volume

Fig. 2

Table 3. Activeness test results

No	Catalyst code	DCM T_{50}, °C	PCE T_{50}, °C	Space velocity h^{-1}	Water %
1	50PtPd(2:1)/AL_2O_3	311	561	28,000	0
2	50Pt/AL_2O_3+0.5Cr	314	537	28,000	0
3	50Pt/AL_2O_3+0.5Cr+3.2V	321	451	28,000	0
4	50Pt/AL_2O_3	290	535	28,000	1.5
5	50Pt/AL_2O_3+3.2V	307	525	28,000	1.5
6	50Pt/AL_2O_3+0.5Cr+3.2V	317	466	28,000	1.5
7	100PtPd(1:4)/AL_2O_3+0.5Cr+3.2V	329	446	28,000	1.5
8	50Pt/AL_2O_3+0.5Cr+3.2V	315	423	14,000	3.0
9	100PtPd(1:4)/AL_2O_3+0.5Cr+3.2V	291	424	14,000	3.0
10	250PtPd(1:4)/AL_2O_3+0.5Cr+3.2V	336	438	28,000	1.5
11	90Pt/AL_2O_3+0.5Cr+3.2V	323	429	28,000	1.5
12	250PtPd(1:4)/AL_2O_3	332	506	28,000	1.5
13	250PtPd(1:4)/AL_2O_3+0.5Cr+3.2V	316	416	14,000	1.5
14	90Pt/AL_2O_3+0.5Cr+3.2V	329	409	14,000	1.5
15	250PtPd(1:4)/AL_2O_3	296	491	14,000	1.5
16	50Pt/AL_2O_3+0.5Cr+3.2V	312	431	14,000	1.5
17	50PtRh(5:1)/AL_2O_3	290	527	28,000	1.5
18	50PtRh(5:1)/AL_2O_3+0.5Cr+3.2V	330	446	28,000	1.5
19	AL_2O_3+0.5Cr+3.2V	355	495	28,000	1.5
20	TiO_2+0.5Cr+3.2V	380	400	28,000	1.5
21	TiO_2+0.5Cr+3.2V+10WO_3	435	365	28,000	1.5
22	50Pt/TiO_2+0.5Cr+3.2V	355	400	28,000	1.5
23	50Pt/TiO_2+0.5Cr+3.2V+10WO_3	400	330	28,000	1.5
24	40Pt/TiO_2+26WO_3	276	353	28,000	1.5
25	40Pt/TiO_2+26WO_3+0.5Cr	255	402	28,000	1.5
26	40Pt/TiO_2+26WO_3+3Fe	299	398	28,000	1.5
27	TiO_2+26WO_3	282	No	28,000	1.5
28	TiO_2+0.5Cr +26WO_3	254	No	28,000	1.5

T_{50} value is the temperature (°C), in which 50% of the compound has reacted. No = not measured.

Fig. 3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/FI2008/050441

A. CLASSIFICATION OF SUBJECT MATTER

See extra sheet

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC8: B01D, B01J

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

FI, SE, NO, DK

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Epo internal, WPI, XPESP

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	JP 61120640 A (NIPPON CATALYTIC CHEM IND) 07 June 1986 (07.06.1986)	
X	Epodoc and WPI abstracts [online].	1-18
Y		19-27
	JP 2007117911 A (SHIMANE PREFECTURE) 17 May 2007 (17.05.2007)	
X	& Epodoc and WPI abstracts [online] & machine translation in English (translated 10.11.2008), paragraphs [0019] and [0030].	1-2, 4-14, 16-18, 28-30
Y		19-27

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:

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

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

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
12 November 2008 (12.11.2008)	14 November 2008 (14.11.2008)

Name and mailing address of the ISA/FI	Authorized officer
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Facsimile No. +358 9 6939 5328	Telephone No. +358 9 6939 500

INTERNATIONAL SEARCH REPORT

International application No.
PCT/FI2008/050441

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

According to PCT rule 13.1., an application shall relate to one invention only or to a group of inventions so linked as to form a single general inventive concept. Further according to Rule 13.2. PCT, the requirement of unity is fulfilled only when there is a technical relationship among claimed inventions involving one or more of the same or corresponding special technical features. The expression "special technical feature" means those technical features that define a contribution which each of the claimed inventions, considered as a whole, makes over the prior art. Independent claims 1, 13 and 19 define a catalyst, a method to manufacture such catalyst and a method to purify halogenated and non-halogenated hydrocarbons with this catalyst. The catalyst is composed of noble metals, vanadium and one or several additives chosen from the group of Cr, Mn, Fe, Co and Ni. The catalyst defined in claim 28 does not contain any of these elements. Furthermore, the catalyst defined in claims 29-30 does not contain vanadium. Hence, the subject of matter of claims 28-30 is not linked with claims 1-27 by one or more of the same corresponding special technical features. Therefore, unity of invention (Rule 13.1 PCT) no longer exists.

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☒ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/FI2008/050441

Patent document cited in search report	Publication date	Patent family members(s)	Publication date
JP 61120640 A	07/06/1986	None	
JP 2007117911 A	17/05/2007	None	

INTERNATIONAL SEARCH REPORT

International application No.
PCT/FI2008/050441

CLASSIFICATION OF SUBJECT MATTER

Int.Cl.
B01J 23/648 (2006.01)
B01J 23/64 (2006.01)
B01D 53/86 (2006.01)
B01D 53/94 (2006.01)