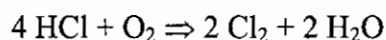


Process for the production of chlorine by gas phase oxidation

The present invention relates to a process for the production of chlorine by catalytic gas phase oxidation of hydrogen chloride with oxygen, wherein the catalyst comprises tin dioxide and at least one halogen-containing ruthenium compound, a catalyst composition and the use thereof.

The process, developed by Deacon in 1868, of the catalytic oxidation of hydrogen chloride with oxygen in an exothermic equilibrium reaction was at the beginning of industrial chlorine chemistry:



However, the Deacon process was largely supplanted by chlor-alkali electrolysis. Virtually the entire production of chlorine was by electrolysis of aqueous sodium chloride solutions (Ullmann Encyclopedia of Industrial Chemistry, seventh release, 2006). However, the attractiveness of the Deacon process has recently been increasing again, since worldwide demand for chlorine is growing faster than the demand for sodium hydroxide solution. The process for the production of chlorine by oxidation of hydrogen chloride, which is unconnected with the preparation of sodium hydroxide solution, satisfies this development. Furthermore, hydrogen chloride is obtained as a linked product in large quantities, for example in phosgenation reactions such as in the preparation of isocyanate.

The oxidation of hydrogen chloride to chlorine is an equilibrium reaction. The position of the equilibrium shifts to the detriment of the desired end product as the temperature increases. It is therefore advantageous to employ catalysts with the highest possible activity, which allow the reaction to proceed at a low temperature.

The first catalysts for oxidation of hydrogen chloride contained copper chloride or oxide as the active component and were already described by Deacon in 1868. However, these had only low activities at low temperatures (< 400°C). By increasing the reaction temperature it was indeed possible to increase the activity,

but a disadvantage was that the volatility of the active components at elevated temperatures led to a rapid decrease in the activity of the catalyst.

5 EP 0 184 413 describes the oxidation of hydrogen chloride with catalysts based on chromium oxides. However, the process realized by this means has an inadequate activity and high reaction temperatures.

10 The first catalysts for the oxidation of hydrogen chloride containing the catalytically active component ruthenium were already described in 1965 in DE 1 567 788. In this case, starting from RuCl_3 supported for example on silicon dioxide and aluminium oxide. However, the activity of these $\text{RuCl}_3/\text{SiO}_2$ catalysts is very low. Further Ru-based catalysts with the active mass of ruthenium oxide or ruthenium mixed oxide and various oxides, such as e.g. titanium dioxide, zirconium dioxide etc., as the support material were claimed in DE-A 197 48 299. In this connection,
15 the content of ruthenium oxide is 0.1 wt.% to 20 wt.% and the average particle diameter of ruthenium oxide is 1.0 nm to 10.0 nm. Further Ru catalysts supported on titanium dioxide or zirconium dioxide are known from DE-A 197 34 412. A number of Ru starting compounds, such as e.g. ruthenium-carbonyl complexes, ruthenium salts of inorganic acids, ruthenium-nitrosyl complexes, ruthenium-amine
20 complexes, ruthenium complexes of organic amines or ruthenium-acetylacetonate complexes, were mentioned for the preparation of the ruthenium chloride and ruthenium oxide catalysts described therein, which contain at least one compound of titanium oxide and zirconium oxide. In a preferred embodiment, TiO_2 in the rutile form was employed as the support. The ruthenium oxide catalysts have a fairly high
25 activity, but their preparation is expensive and requires a number of operations, such as precipitation, impregnation with subsequent precipitation etc., the scale-up of which is difficult industrially. In addition, at high temperatures Ru oxide catalysts also tend to sinter and thus tend to undergo deactivation.

30 EP 0 936 184 A2 describes a process for the catalytic oxidation of hydrogen chloride, wherein the catalyst is chosen from an extensive list of possible catalysts. Among the catalysts is the variant designated number (6), which consists of the active component (A) and a component (B). The component (B) is a compound

component which has a certain thermal conductivity. Tin dioxide inter alia is mentioned as an example. In addition the component (A) can be absorbed on to a support. However, possible supports do not include tin dioxide. There is also not a single example in which tin dioxide was used. Furthermore, exclusively the use of
5 ruthenium oxide as a catalyst component is described in this patent. This is prepared in particular by impregnation of the support with a ruthenium chloride solution, precipitation of the ruthenium hydroxide on the support and subsequent calcining. The document mentioned consequently discloses neither the use of tin dioxide as a catalyst support in the catalytic gas phase oxidation of hydrogen chloride with
10 oxygen, nor the use of a halogen-containing ruthenium compound as a catalyst component.

The catalysts developed to date for the Deacon process have a number of inadequacies. At low temperatures their activity is inadequate. It was indeed
15 possible to increase the activity by increasing the reaction temperature, but this led to sintering/deactivation or to a loss of the catalytic component.

The object of the present invention was to provide a catalytic system which effects the oxidation of hydrogen chloride at low temperatures and with high activities.
20 This object is achieved by the development of a quite specific combination of catalytically active components and a specific support material.

It has been found surprisingly that by the targeted supporting of a halogen-containing ruthenium compound on tin dioxide, due to a particular interaction
25 between the catalytically active component and support novel highly active catalysts are provided which have a high catalytic activity in the oxidation of hydrogen chloride, especially at temperatures of $\leq 350^{\circ}\text{C}$. A further advantage of the catalyst system according to the invention is the simple application, which is easy to scale up, of the catalytically active component to the support. Furthermore, a conversion
30 of the catalytically active halogen-containing species to the oxide is omitted.

The present invention thus provides a process for the production of chlorine by catalytic gas phase oxidation of hydrogen chloride with oxygen, wherein the catalyst

comprises at least tin dioxide and at least one halogen-containing ruthenium compound.

5 In a preferred embodiment tin(IV) oxide is employed as the support for the catalytically active component, particularly preferably tin dioxide in the rutile structure.

According to the invention a halogen-containing ruthenium compound is used as the catalytically active component. This is a compound in which halogen is bonded in
10 ionic to polarized covalent form to a ruthenium atom.

The halogen in the halogen-containing ruthenium compound is preferably chosen from the group which consists of chlorine, bromine and iodine. Chlorine is preferred.

15 The halogen-containing ruthenium compound includes those which consist exclusively of halogen and ruthenium. However, those which contain both oxygen and halogen, in particular chlorine or chloride, are preferred. At least one ruthenium oxychloride compound is particularly preferably used as the catalytically active
20 species. A ruthenium oxychloride compound in the context of the invention is a compound in which both oxygen and chlorine are present bonded in ionic to polarized covalent form to ruthenium. Such a compound thus has the general composition RuO_xCl_y . According to the invention, various such ruthenium oxychloride compounds can be present side by side in the catalyst. Examples of
25 defined ruthenium oxychloride compounds include in particular the following compositions: Ru_2OCl_4 , RuOCl_2 , Ru_2OCl_5 and Ru_2OCl_6 .

In a particularly preferred process the halogen-containing ruthenium compound is a mixed compound corresponding to the general formula RuCl_xO_y , wherein x denotes
30 a number from 0.8 to 1.5 and y denotes a number from 0.7 to 1.6.

The catalytically active ruthenium oxychloride compound in the context of the invention is preferably obtainable by a process which comprises first of all the

application of an aqueous solution or suspension of at least one halogen-containing ruthenium compound to tin dioxide, and the removal of the solvent.

Other conceivable processes include the chlorination of ruthenium compounds which do not contain chlorine, such as ruthenium hydroxides, before or after absorption on to the support.

A preferred process includes the application of an aqueous solution of RuCl_3 to the tin dioxide.

The application includes in particular the impregnation of the optionally freshly precipitated tin dioxide with the solution of the halogen-containing ruthenium compound.

After the application of the halogen-containing ruthenium compound, a drying step which is expediently carried out in the presence of oxygen or air in general takes place, in order to render possible at least in part a conversion into the preferred ruthenium oxychloride compounds. In order to avoid a conversion of the preferred ruthenium oxychloride compounds to ruthenium oxides, the drying should preferably be carried out at below 280°C , in particular at a temperature of at least 80°C , particularly preferably at least 100°C .

A preferred process is characterised in that the catalyst can be obtained by calcining a tin dioxide support charged with a halogen-containing ruthenium compound, at a temperature of at least 200°C , preferably at least 220°C , particularly preferably at least 250°C to 500°C , in particular in an oxygen-containing atmosphere, particularly preferably under air.

In a particularly preferred process the proportion of ruthenium from the halogen-containing ruthenium compound in relation to the overall catalyst composition, in particular after the calcining, is 0.5 to 5 wt.%, preferably 1.0 to 3 wt.%, particularly preferably 1.5 to 3 wt.%.

If halogen-ruthenium compounds which contain no oxygen are to be absorbed as the catalytically active species, drying can also be carried out at higher temperatures with exclusion of oxygen.

- 5 The substantial conversion of the halogen-ruthenium compound into the preferred ruthenium oxyhalide compounds is preferably carried out in the reactor under the conditions of the oxidation process. The evaluation of the lattice interplanar spacings in the HR-TEM (high resolution transmission electron microscopy) of a ruthenium chloride-SnO₂ catalyst thus shows that this is converted into ruthenium
10 oxychloride under the conditions of the gas phase oxidation of hydrogen chloride.

Preferably, the catalyst is obtainable by a process which comprises the application of an aqueous solution or suspension of at least one halogen-containing ruthenium compound to tin dioxide and subsequent drying at below 280°C, and subsequent
15 activation under the conditions of the gas phase oxidation of hydrogen chloride, during which a substantial conversion to the ruthenium oxychlorides takes place. The longer the drying in the presence of oxygen, the more oxychloride is formed.

The loading of the catalytically active component, i.e. the halogen-containing
20 ruthenium compound, is normally in the range 0.1-80 wt.%, preferably in the range 1-50 wt.%, particularly preferably in the range 1-20 wt.%, based on the total weight of the catalyst (catalyst component and support).

Particularly preferably the catalytic component, i.e. the halogen-containing
25 ruthenium compound, can be applied to the support by for example moist and wet impregnation of a support with suitable starting compounds present in solution or starting compounds in liquid or colloidal form, precipitation and co-precipitation processes, as well as ion exchange and gas phase coating (CVD, PVD).

30 Possible promoters are metals which have a basic action, for example alkali, alkaline earth and rare earth metals, preferably alkali metals, in particular Na and Cs, and alkaline earth metals, particularly preferably alkaline earth metals, especially Sr and Ba.

The promoters can be applied to the catalyst by impregnation and CVD processes, without being limited thereto, an impregnation being preferred, particularly preferably after application of the catalytic main component.

5

For stabilization of the dispersion of the catalytic main component on the support, various dispersion stabilizers, such as for example scandium oxides, manganese oxides and lanthanum oxides etc., can for example be employed, without being limited thereto. The stabilizers are preferably applied by impregnation and/or precipitation together with the catalytic main component.

10

The tin dioxide used according to the invention is commercially obtainable (e.g. from Chempur, Alfa Aesar) or can be obtained for example by alkaline precipitation of tin(IV) chloride and subsequent drying. It has in particular BET surface areas of from about 1 to 300 m²/g.

15

The tin dioxide used as the support according to the invention can undergo a reduction in the specific surface area under exposure to heat (such as at temperatures of more than 250°C), which can be accompanied by a reduction in the activity of the catalyst. The pretreatment of the SnO₂ support can be effected by a calcination for example at 250-1500°C, but particularly preferably at 300-1200°C. The aforementioned dispersion stabilizers can also serve to stabilize the surface of the tin dioxide at high temperatures.

20

A further preferred process is in fact characterised in that the reaction temperature in the catalytic gas phase oxidation is up to 450°C, preferably at most 420°C.

25

The catalysts can be dried under normal pressure or preferably under reduced pressure, preferably at 40 to 200°C. The duration of the drying is preferably 10 min to 6 h.

30

The catalysts according to the invention for the oxidation of hydrogen chloride are distinguished by a high activity at low temperatures.

Preferably, as described above, the new catalyst composition is used in the catalytic process known as the Deacon process. Here, hydrogen chloride is oxidised with oxygen in an exothermic equilibrium reaction to give chlorine, steam being formed.

5 The reaction temperature is usually 180° to 500°C, preferably 200° to 400°C, particularly preferably 220° to 350°C, and the normal reaction pressure is 1 to 25 bar, preferably 1.2 to 20 bar, particularly preferably 1.5 to 17 bar, most particularly preferably 2 to 15 bar. Since an equilibrium reaction is involved, it is expedient to operate at temperatures as low as possible at which the catalyst still exhibits a
10 sufficient activity. Furthermore it is expedient to use oxygen in hyperstoichiometric amounts relative to hydrogen chloride. For example a two-fold to four-fold oxygen excess is usually employed. Since there is no danger of loss of activity, it may be economically advantageous to operate at a relatively high pressure and accordingly at a longer residence time than under normal pressure.

15

Suitable preferred catalysts for the Deacon process, which can be combined with the new catalyst support, contain ruthenium oxide, ruthenium chloride or other ruthenium compounds on silicon dioxide, aluminium oxide, titanium dioxide or zirconium dioxide as support.

20

Suitable catalysts can contain in addition to a ruthenium compound, also compounds of other noble metals, for example gold, palladium, platinum, osmium, iridium, silver, copper or rhenium. Suitable catalysts can furthermore contain chromium (III) oxide.

25

The catalytic hydrogen chloride oxidation can preferably be carried out adiabatically or isothermally or approximately isothermally, batchwise but preferably continuously, as a fluidised bed or fixed bed process, preferably as a fixed bed process, particularly preferably in shell-and-tube reactors on heterogeneous catalysts
30 at a reactor temperature of 180° to 500°C, preferably 200° to 400°C, particularly preferably 220° to 350°C, and at a pressure of 1 to 25 bar (1,000 to 25,000 hPa), preferably 1.2 to 20 bar, particularly preferably 1.5 to 17 bar and especially 2.0 to 15 bar.

Conventional reaction apparatuses in which the catalytic hydrogen chloride oxidation is carried out are fixed bed or fluidised bed reactors. The catalytic hydrogen chloride oxidation can preferably also be carried out in several stages.

5

In the adiabatic, isothermal or approximately isothermal procedure several, i.e. 2 to 10, preferably 2 to 6, particularly preferably 2 to 5 and especially 2 to 3, reactors connected in series with intermediate cooling can be used. The oxygen can either be added in total together with the hydrogen chloride upstream of the first reactor, or
10 can be added distributed over the various reactors. This series arrangement of individual reactors can also be combined in one apparatus.

A further preferred embodiment of an arrangement suitable for the process consists in the use of a structured catalyst packing, in which the catalyst activity increases in
15 the flow direction. Such a structuring of the catalyst packing can be achieved by different degrees of impregnation of the catalyst support with active material or by different dilution of the catalyst with an inert material. As inert material there may for example be used rings, cylinders or spheres of tin dioxide, titanium dioxide, zirconium dioxide or mixtures thereof, aluminium oxide, steatite, ceramics, glass,
20 graphite or stainless steel. With the preferred use of catalyst moulded articles the inert material should preferably have similar external dimensions.

Moulded articles of arbitrary shapes are suitable as catalyst moulded articles, tablets, rings, cylinders, stars, wagon wheels or spheres being preferred, and rings,
25 cylinders, spheres or star-shaped strands being particularly preferred. A spherical shape is preferred. The size of the catalyst moulded articles, for example diameter in the case of spheres, or maximum cross-sectional width, is on average in particular 0.3 to 7 mm, most particularly preferably 0.8 to 5 mm.

30 As an alternative to the finely particulate catalyst moulded articles described above, the support can also be a monolith of support material, for example not only a "conventional" support body with parallel channels not radially connected to one another; foams, sponges or the like with three-dimensional connections within the

support body are also counted as monoliths, as well as support bodies with cross-stream channels.

5 The monolithic support can have a honeycomb structure, but also an open or closed cross-channel structure. The monolithic support has a preferred cell density of 100 to 900 cells per square inch (cps), particularly preferably 200 to 600 cps.

10 A monolith in the context of the present invention is disclosed for example in "Monoliths in multiphase catalytic processes – aspects and prospects" by F. Kapteijn, J.J. Heiszwolf T.A. Nijhuis and J.A. Moulijn, Cattech 3, 1999, p. 24.

15 Suitable additional support materials or binders for the support include especially for example silicon dioxide, graphite, titanium dioxide in the rutile or anatase structure, zirconium dioxide, aluminium oxide or their mixtures, preferably titanium dioxide, zirconium dioxide, aluminium oxide or their mixtures, particularly preferably γ - or δ - aluminium oxide or their mixtures. A preferred binder is aluminium oxide or zirconium oxide. The proportion of binder referred to the finished catalyst can be 1 to 70 wt.%, preferably 2 to 50 wt.% and most particularly preferably 5 to 30 wt.%. The binder increases the mechanical stability (strength) of the catalyst moulded
20 articles.

In a particularly preferred variant of the invention the catalytically active component is present substantially on the surface of the actual support material, for example tin oxide, but not on the surface of the binder.

25 Suitable promoters for additional doping of the catalysts are alkali metals such as lithium, sodium, potassium, rubidium and caesium, preferably lithium, sodium and potassium, particularly preferably potassium, alkaline earth metals such as magnesium, calcium, strontium and barium, preferably magnesium and calcium, particularly preferably magnesium, and rare earth metal such as scandium, yttrium,
30 lanthanum, cerium, praseodymium and neodymium, preferably scandium, yttrium, lanthanum and cerium, particularly preferably lanthanum and cerium, or their mixtures.

The conversion of hydrogen chloride in a simple pass can preferably be restricted to 15 to 90%, preferably 40 to 85%, particularly preferably 50 to 70%. Unreacted hydrogen chloride can, after separation, be recycled partially or completely to the catalytic hydrogen chloride oxidation. The volume ratio of hydrogen chloride to oxygen at the reactor inlet is preferably 1:1 to 20:1, more preferably 2:1 to 8:1, particularly preferably 2:1 to 5:1.

The heat of reaction of the catalytic hydrogen chloride oxidation can advantageously be used to generate high-pressure steam. This can be utilised to operate a phosgenation reactor or distillation columns, in particular isocyanate distillation columns.

The formed chlorine is separated in a further step. The separation step normally comprises several stages, namely the separation and optional recycling of unreacted hydrogen chloride from the product gas stream to the catalytic hydrogen chloride oxidation, the drying of the obtained stream, containing substantially chlorine and oxygen, as well as the separation of chlorine from the dried stream.

The separation of unreacted hydrogen chloride and of formed steam can be effected by condensing out aqueous hydrochloric acid from the product gas stream of the hydrogen chloride oxidation by cooling. Hydrogen chloride can also be absorbed in dilute hydrochloric acid or water.

The invention also provides for the use of tin dioxide as catalyst support for a catalyst in the catalytic gas phase oxidation of hydrogen chloride with oxygen.

The invention furthermore provides a catalyst composition that includes tin dioxide and at least one halogen-containing ruthenium compound.

A composition is preferred which is characterised in that the halogen is selected from chlorine, bromine and iodine.

The halogen-containing ruthenium compound includes particularly preferably a ruthenium oxychloride compound.

5 Most particularly preferably the halogen-containing ruthenium compound is a mixed compound corresponding to the general formula RuCl_xO_y , wherein x denotes a number from 0.8 to 1.5 and y denotes a number from 0.7 to 1.6.

10 The catalyst composition can preferably be obtained by a process which involves the application of an in particular aqueous solution or suspension of at least one halogen-containing ruthenium compound to tin dioxide and the removal of the solvent.

15 In this connection the halogen-containing ruthenium compound is particularly preferably RuCl_3 .

The catalyst composition can in particular be obtained by a process which involves the application of an aqueous solution or suspension of at least one halogen-containing ruthenium compound to tin dioxide and the subsequent drying at a temperature of at least 80°C, preferably at least 100°C.

20 The catalyst composition is in particular preferably obtainable by a process in which a tin dioxide support loaded with a halogen-containing ruthenium compound is calcined at a temperature of at least 200°C, preferably at least 240°C, particularly preferably at least 270°C to 500°C, in particular in an oxygen-containing atmosphere, particularly preferably under air.

25 The proportion of the halogen-containing ruthenium compound in relation to the overall catalyst composition is, particularly after the calcination, 0.5 to 5 wt.%, preferably 1.0 to 3 wt.%.

30 The invention also provides for the use of the catalyst composition as a catalyst, in particular for oxidation reactions, particularly preferably as a catalyst in the catalytic gas phase oxidation of hydrogen chloride with oxygen.

The following examples illustrate the present invention:

Examples

5 Example 1 (invention)

Supporting of ruthenium chloride on SnO₂

20 g of commercially available tin(IV) oxide (Chempur; with a BET surface area of
10 4.4 m²/g) were suspended in a solution of 2.35 g of commercially obtainable
ruthenium chloride n-hydrate in 50 ml of water in a round-bottomed flask with a
dropping funnel and reflux condenser and the mixture was stirred for 180 min at
room temperature and then for 120 min at 65°C. The excess solution was filtered off
and the moist solid was dried at 120°C in a vacuum drying cabinet for 4 h, and in
15 each case 5 g were then dried for 3 h at 250°C in a stream of air, a ruthenium
chloride catalyst supported on tin(IV) oxide being obtained. The amount of Ru
determined by elemental analysis (ICP-OES) was 4.1 wt.%, and that of Cl was
1.1 wt.%.

20 Example 2 (invention):

20 g of commercially available tin(IV) oxide (Sigma-Aldrich; BET surface of
15m²/g) were suspended in a solution of 2.35 g of commercially obtainable
ruthenium chloride n-hydrate in 50 ml of water in a round-bottomed flask equipped
25 with a dropping funnel and reflux condenser, and stirred for 60 minutes at room
temperature. The water is then separated in an air stream at 60°C. The calcinations
was carried out for 16 hours at 250°C in an air stream, a ruthenium chloride catalyst
supported on tin(IV) oxide being obtained. The amount of Ru determined by
elemental analysis (ICP-OES) was 3.8 wt.%, and that of Cl was 1.6 wt.%.

Example 3 (comparison):**Supporting of ruthenium chloride on silica gel (SiO₂)**

5

In accordance with the process in Example 1, a catalyst of ruthenium chloride on silicon dioxide (silica gel 100, Merck) was prepared and was calcined for 3 h at 250°C in a stream of air. The amount of Ru determined by elemental analysis (ICP-OES) was 4.1 %, and that of Cl was 0.8 wt.%.

10

Example 4 (comparison):**Supporting of ruthenium oxide on titanium dioxide (TiO₂)**

15

20 g of support (titanium oxide: manufacturer Sachtleben; BET surface of 90m²/g) were suspended at room temperature in a 1 litre capacity three-necked flask and stirred with a magnetic stirrer. 1.93 g of ruthenium chloride n-hydrate were dissolved in 50 ml of water and added to the suspension. The suspension was then stirred for 30 minutes. Following this 24 g of 10% sodium hydroxide solution were added dropwise within 15 minutes and the mixture was stirred for a further 30 minutes. A further 12 g of 10% sodium hydroxide solution were then added dropwise in 10 minutes. The reaction mixture was then heated to 65°C and held for one hour at this temperature, and then cooled to 40°C while stirring. The suspension was next filtered and the solid was washed five times with 50 ml of water. The moist solid was dried for 4 hours at 120°C in a vacuum drying cabinet and then calcined in a muffle-type furnace for 2 hours at 300°C. The amount of Ru determined by elemental analysis (ICP-OES) was 4.0 wt.% and that of Cl was < 0.2 wt.%.

20

25

Example 5 (reference):**Blank experiment with tin dioxide**

- 5 As a blank experiment, tin dioxide was used instead of a catalyst and was tested as described below. The small amount of chlorine produced is to be attributed to the gas phase reaction.

Catalyst tests Examples 1-5

10

Use of the catalysts in the oxidation of HCl

- 15 A gas mixture of 80 ml/min (STP) of hydrogen chloride and 80 ml/min (STP) of oxygen flowed through the catalysts from Examples 1 to 5 in a packed fixed bed in a quartz reaction tube (internal diameter 10 mm) at 300°C. The quartz reaction tube was heated by an electrically heated fluidized bed of sand. After 30 min the product gas stream was passed into 16 % strength potassium iodide solution for 10 min. The iodine formed was then back-titrated with 0.1 N thiosulfate standard solution in order to determine the amount of chlorine passed in. Table 1 shows the results.

20

Table 1: Activity in the oxidation of HCl

Example	Composition	Ru wt. %	Cl wt. %	Chlorine formation mmol/min.g (cat)	Chlorine formation mmol/min.g (Ru)
1	RuCl ₃ /SnO ₂	4.1	1.1	0.35	8.5
2	RuCl ₃ /SnO ₂	3.8	1.6	0.89	23.4
3 (comp.)	RuCl ₃ /SiO ₂	4.1	0.8	0.15	3.8
4 (comp.)	RuO ₂ /TiO ₂	4.0	< 0.2	0.55	13.7
5 (ref.)	SnO ₂	-	-	(0.08)	-

Long-term study: Long-term stability of catalyst supported on tin oxide

The catalyst from Example 1 was tested as described above, but the time of the experiment was lengthened and several samples were taken by passing them into 16 % strength potassium iodide solution for 10 minutes. The amounts of chlorine shown in Figure 1 are found.

Example 6

4.994 g of commercially available ruthenium chloride n-hydrate were dissolved in 16.62 g of H₂O. 100 g of spherical SnO₂ moulded articles with an average diameter of 1.9 mm, a BET surface of 45.1 m²/g and 15 wt.% Al₂O₃ as binder were added to the solution and thoroughly mixed until the solution had been completely absorbed by the support. After standing time of 1 hour the solid was dried overnight at 60°C in an air stream. The catalyst was then calcined for 16 hours at 250°C. The amount of Ru determined by elemental analysis (ICP-OES) was 1.9 wt.%, and that of Cl was 0.5 wt.%.

In an electron microscopy image / analysis (EDX) it was found that the catalytically active species (ruthenium oxychloride) is contained only on the tin oxide but not on the surface of the aluminium oxide (binder).

Catalyst test Example 6

Use of the catalysts in the HCl oxidation

25 g of the catalyst from Example 6 were incorporated together with 75 g of uncoated support in a nickel fixed-bed reactor (diameter 10 mm, length 800 mm). A fixed bed packing of ca. 150 mm was thereby obtained. A gas mixture of 56 l/hour (STP) of hydrogen chloride and 28 l/hour (STP) of oxygen flowed through the fixed bed packing at 300°C and at a pressure of 4 bar. The Ni reactor was heated by means of a heat carrier medium. After 30 minutes the product gas stream was

passed for 5 minutes into 16% potassium iodide solution. The iodine formed was then back-titrated with 0.1 N thiosulfate standard solution in order to determine the introduced amount of chlorine. The catalyst activity calculated therefrom was 0.40 kg_{Cl₂}/kg_{CAT}·h.

5

The addition of aluminium oxide as binder furthermore obviously imparted a greater strength to the spherical catalyst than comparable moulded articles that consist merely of tin oxide on support material.

10

Example 7

Sn coating

15 20 g of aluminium oxide moulded articles (hollow extrudate, 4 x 9 mm, Sasol) were placed in a Erlenmeyer flask cooled with iced water, coated with 93.34 g of SnCl₄ and left to stand for 30 minutes. The SnCl₄ was then decanted off into a second Erlenmeyer flask. The moulded articles were covered with 150 ml of water via a dropping funnel and left to stand for 30 minutes. The moulded articles coated in this
20 way were washed with water until neutral and then dried at 60°C/10 mbar in a drying cabinet to constant weight (21.51 g). This procedure was repeated once more. 5g of the moulded article were then calcined for 4 hours at 750°C in a muffle furnace.

25

Example 8

Ru impregnation

30 0.078 g of ruthenium chloride n-hydrate (Heraeus) was dissolved in 0.39 ml of water and 2.5 g of the support produced in Example 7 was added thereto and mixed thoroughly until the solution had been absorbed by the support. The impregnation time was 1.5 hours. The moist solid was then dried at 60°C in an oven (air oven) for

ca. 5 hours. The yield was 2.615 g. The ruthenium-containing catalyst prepared in this way was then calcined for 16 hours at 250°C in a muffle furnace. The ruthenium content was 1.1 wt.% referred to the catalyst material.

- 5 Figure 2 shows a scanning electron microscopy image of the extrudate cross-section. Figures 3 and 4 show respectively the tin and ruthenium distributions of this section. With regard to the support-free image sections the uniform distribution of the ruthenium in the support extrudate can be recognised.

10

Catalyst test Example 8

Use of the catalysts in the HCl oxidation

- 15 Catalytic tests

20

A gas mixture of 80 ml/min (STP) of hydrogen chloride and 80 ml/min (STP) of oxygen flowed at 300°C through the catalyst of Example 8 in a fixed-bed packing in a quartz reaction tube (diameter 10 mm). The quartz reaction tube was heated by an electrically heated fluidised sand layer. After 30 minutes the product gas stream was passed for 10 minutes into 16% potassium iodide solution. The iodine formed was then back-titrated with 0.1 N thiosulfate standard solution in order to determine the amount of chlorine introduced. A space-time yield of 1.46 kg_{Cl₂}/kg_{Cat}.h was found.

Patent claims:

1. Process for the production of chlorine by catalytic gas phase oxidation of hydrogen chloride with oxygen, characterised in that the catalyst comprises at least tin dioxide and at least one halogen-containing ruthenium compound.
5
2. Process according to claim 1, characterised in that a halogen from the series chlorine, bromine and/or iodine is selected as halogen.
- 10 3. Process according to claim 1 or 2, characterised in that the halogen-containing ruthenium compound comprises a ruthenium oxychloride compound.
- 15 4. Process according to claim 3, characterised in that the halogen-containing ruthenium compound is a compound corresponding to the general formula RuCl_xO_y , wherein x denotes a number from 0.8 to 1.5 and y denotes a number of 0.7 to 1.6.
- 20 5. Process according to one of claims 1 to 4, characterised in that the catalyst is obtainable by a process which includes the application of an in particular aqueous solution or suspension of at least one halogen-containing ruthenium compound to tin dioxide and the removal of the solvent.
- 25 6. Process according to claim 5, characterised in that the halogen-containing ruthenium compound is RuCl_3 .
- 30 7. Process according to claim 5 or 6, characterised in that the catalyst is obtainable by a process which includes the application of an aqueous solution or suspension of at least one halogen-containing ruthenium compound to tin dioxide and the subsequent drying at a temperature of at least 80°C, preferably at least 100°C.

8. Process according to one of claims 1 to 7, characterised in that the catalyst can be obtained by calcining a tin dioxide support loaded with a halogen-containing ruthenium compound, at a temperature of at least 200°C, preferably at least 220°C, particularly preferably at least 250°C to 500°C, in particular in an oxygen-containing atmosphere, particularly preferably under air.
9. Process according to one of claims 1 to 8, characterised in that the proportion of ruthenium from the halogen-containing ruthenium compound in relation to the overall catalyst composition, in particular after the calcinations, is 0.5 to 5 wt.%, preferably 1.0 to 3 wt.%, particularly preferably 1.5 to 3 wt.%.
10. Process according to one of claims 1 to 9, characterised in that the tin dioxide is present at least partially, preferably completely, in the rutile form.
11. Process according to one of claims 1 to 10, characterised in that the gas phase oxidation of the hydrogen chloride includes passing over a gas containing hydrogen chloride and oxygen at a temperature of 180° to 500°C, preferably 200° to 450°C, particularly preferably 220° to 380°C.
12. Process according to one of claims 1 to 11, characterised in that the gas phase oxidation is carried out at a pressure of 1 to 25 bar, preferably 1.2 to 20 bar, particularly preferably 1.5 to 17 bar and especially preferably 2.0 to 15 bar.
13. Process according to one of claims 1 to 12, characterised in that the gas phase oxidation is carried out adiabatically or isothermally, in particular adiabatically.
14. Use of tin dioxide as catalyst support for a catalyst in the catalytic gas phase oxidation of hydrogen chloride with oxygen.

15. Catalyst composition that contains tin dioxide and at least one halogen-containing ruthenium compound.
- 5 16. Composition according to claim 15, characterised in that the halogen is selected from the series chlorine, bromine and iodine.
17. Composition according to claim 15 or 16, characterised in that the halogen-containing ruthenium compound contains a ruthenium oxychloride compound.
- 10 18. Composition according to claim 17, characterised in that the halogen-containing ruthenium compound is a mixed compound corresponding to the general formula RuCl_xO_y , wherein x denotes a number from 0.8 to 1.5 and y denotes a number from 0.7 to 1.6.
- 15 19. Composition according to one of claims 15 to 18, characterised in that the catalyst is obtainable by a process which includes the application of an in particular aqueous solution or suspension of at least one halogen-containing ruthenium compound to tin dioxide and the removal of the solvent.
- 20 20. Composition according to claim 19, characterised in that the halogen-containing ruthenium compound is RuCl_3 .
- 25 21. Composition according to claim 19 or 20, characterised in that the catalyst is obtainable by a process that includes the application of an aqueous solution or suspension of at least one halogen-containing ruthenium compound to tin dioxide and the subsequent drying at a temperature of at least 80°C, preferably at least 100°C.
- 30 22. Composition according to one of claims 15 to 21, characterised in that the catalyst can be obtained by calcining a tin dioxide support loaded with a halogen-containing ruthenium compound, at a temperature of at least 200°C, preferably at least 220°C, particularly preferably at least 250° to 500°C,

especially in an oxygen-containing atmosphere, particularly preferably under air.

- 5 23. Composition according to one of claims 15 to 22, characterised in that the proportion of the halogen-containing ruthenium compound in relation to the overall catalyst composition, in particular after the calcination, is 1 to 5 wt.%, preferably 1.5 to 3 wt.%.
- 10 24. Composition according to one of claims 15 to 23, characterised in that this comprises a binder for the support which is selected from the series: silicon dioxide, graphite, titanium dioxide of rutile or anatase structure, zirconium dioxide, aluminium oxide or their mixtures, preferably titanium dioxide, zirconium dioxide, aluminium oxide or their mixtures, particularly preferably aluminium oxide or zirconium oxide, and in which the proportion of binder referred to the finished catalyst is preferably 1 to 70 wt.%, particularly 15 preferably 2 to 50 wt.%, and most particularly preferably 5 to 30 wt.%.
25. Use of the composition according to one of claims 15 to 24 as a catalyst.
- 20 26. Use according to claim 25 as a catalyst for oxidation reaction.
27. Use according to claim 25 or 26 as a catalyst in the catalytic gas phase oxidation of hydrogen chloride with oxygen.