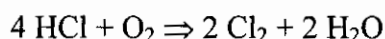


Process for the production of chlorine by gas phase oxidation

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

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:

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However, the Deacon process was pushed severely into the background by chlor-alkali electrolysis. Virtually the entire production of chlorine was by electrolysis of aqueous sodium chloride solutions (Ullmann Encyclopedia of Industrial Chemistry,
15 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
20 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
25 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 the oxidation of hydrogen chloride contained copper chloride
30 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 1567788. In this case, starting from RuCl_3 e.g. supported 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 19748299. In this, the content of ruthenium oxide is 15 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 19734412. A number of Ru starting compounds, such as e.g. ruthenium-carbonyl complexes, ruthenium salts of inorganic acids, ruthenium-nitrosyl complexes, ruthenium-amine complexes, ruthenium complexes 20 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 quite high activity, but the use thereof is 25 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 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). Component (B) is a compound

component which has a certain thermal conductivity. Tin dioxide, inter alia, is mentioned as an example. In addition, component (A) can be absorbed on a support. However, possible supports do not include tin dioxide. There is also not a single example in which tin dioxide was used.

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

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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. The object is achieved by the development of a quite specific combination of catalytically active components and a specific support material.

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It has been found, surprisingly, that by the targeted supporting of an oxygen-containing ruthenium compound on tin dioxide, due to a particular interaction 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.

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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 tin dioxide and at least one oxygen-containing ruthenium compound. The present invention also provides a catalyst for gas phase oxidation based on tin dioxide as support material and an oxygen-containing ruthenium compound.

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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.

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

5 The catalytically active preferred ruthenium oxyhalide compound in the context of the invention is preferably obtainable by a process which comprises initially the application of an aqueous solution or suspension of at least one halide-containing, e.g. chloride-containing, ruthenium compound to tin dioxide and the subsequent precipitation and optionally the calcining of the precipitated product.

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The precipitation can be carried out under alkaline conditions with direct formation of the oxygen-containing ruthenium compound. It can also be carried out under reducing conditions with primary formation of metallic ruthenium, which is then calcined while oxygen is fed in, whereby the oxygen-containing ruthenium compound is formed.

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Alternatively, the oxygen-containing ruthenium compound can also be obtained by applying metallic ruthenium to tin dioxide followed by oxidation of the ruthenium metal in an oxygen-containing gas, or in particular by exposing the metallic ruthenium on tin dioxide to a gas composition of the educt gases for a Deacon reaction, in other words gases containing at least HCl and oxygen. For example, ruthenium is applied as metal to tin dioxide by means of CVD or MOCVD processes.

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25 A particularly preferred process includes the application of an aqueous solution of ruthenium chloride to the tin dioxide.

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

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After the application of the halide-containing ruthenium compound, a precipitation and a drying or calcining step, which is expediently carried out in the presence of oxygen or air at temperatures of up to 650°C, in general takes place.

- 5 The loading of the catalytically active component, i.e. the oxygen-containing ruthenium compound, is normally in the range 0.1-80 wt.%, preferably in the range of 1-50 wt.%, particularly preferably in the range of 1-20 wt.%, based on the total weight of the catalyst (catalyst component and support).
- 10 Particularly preferably, the catalytic component, i.e. the oxygen-containing 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).
- 15 Possible promoters are metals having a basic action (e.g. 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.
- 20 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.
- For stabilization of the dispersion of the catalytic main component on the support,
- 25 various dispersion stabilizers, such as for example scandium oxides, manganese oxides and lanthanum oxides etc., can be employed, without being limited thereto. The stabilizers are preferably applied by impregnation and/or precipitation together with the catalytic main component.
- 30 The tin dioxide used according to the invention is commercially obtainable (e.g. from Chempur, Alfa Aesar), or is obtainable for example by alkaline precipitation of tin(IV) chloride and subsequent drying. It has in particular BET surface areas of about 1 to 300 m²/g.

The tin dioxide used as the support according to the invention can undergo a reduction in the specific surface area by 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 abovementioned dispersion stabilizers can also serve to stabilize the surface of the tin dioxide at high temperatures.

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.

Preferably the new catalyst is, as described, above employed in the catalytic process known as the Deacon process. Here, hydrogen chloride is oxidised with oxygen in an exothermic equilibrium reaction to chlorine, steam being formed. The reaction temperature is usually 150° to 500°C, and the normal reaction pressure is 1 to 25 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 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.

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.

The catalytic hydrogen chloride oxidation can be carried out adiabatically or preferably 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 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.

- 5 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.

10 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 also be used. The oxygen can either be added in total together with the hydrogen chloride upstream of the first reactor, or can be added distributed over the various reactors. This series arrangement of individual reactors can also be combined in one apparatus.

15 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 the flow direction. Such a structuring of the catalyst packing can be achieved by different degrees of impregnation of the catalyst support with active composition or
20 by different dilutions of the catalyst with an inert material. As inert material there may for example be used rings, cylinders or spheres of titanium dioxide, zirconium dioxide or mixtures thereof, aluminium oxide, steatite, ceramics, glass, graphite or stainless steel. With the preferred use of catalyst moulded articles the inert material should preferably have similar external dimensions.

25 Moulded articles of arbitrary shapes are suitable as catalyst moulded articles, preferred shapes being tablets, rings, cylinders, stars, wagon wheels or spheres, rings, cylinders or star-shaped strands being particularly preferred.

30 Suitable support materials that can be combined with tin dioxide are for example silicon dioxide, graphite, titanium dioxide of rutile or anatase structure, zirconium dioxide, aluminium dioxide or their mixtures, preferably titanium dioxide, zirconium

dioxide, aluminium oxide or their mixtures, particularly preferably γ or δ aluminium oxide or their mixtures.

5 Suitable promoters for doping 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, lanthanum, cerium, praseodymium and neodymium, preferably scandium, yttrium, lanthanum and
10 cerium, particularly preferably lanthanum and cerium, or their mixtures.

The moulded articles can then be dried and optionally calcined at a temperature of 100° to 400°C, preferably 100° to 300°C, for example under a nitrogen, argon or air atmosphere. The moulded articles are preferably first dried at 100° to 150°C and
15 then calcined at 200° to 400°C.

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
20 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
25 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
30 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.

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

10 The following examples illustrate the present invention:

Examples

Example 1: Supporting of ruthenium oxide on tin(IV) oxide

5 20 g of commercially available tin(IV) oxide 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 30 min. 24 g of 10 % strength sodium hydroxide solution were then added dropwise in the course of 30 min and the mixture was stirred for 30 min. A
10 further 12 g of 10 % strength sodium hydroxide solution were subsequently added dropwise in the course of 15 min and the reaction mixture was heated to 65°C and kept at this temperature for 1 h. After cooling, the suspension was filtered and the solid was washed 5 times with 50 ml of water. The moist solid was dried at 120°C in a vacuum drying cabinet for 4 h and then calcined at 300°C in a stream of air, a
15 ruthenium oxide catalyst supported on tin(IV) oxide being obtained. The calculated amount of ruthenium was $\text{Ru}/(\text{RuO}_2 + \text{SnO}_2) = 4.7 \text{ wt.}\%$.

Example 2: Supporting of ruthenium oxide on titanium(IV) oxide (comparison)

20 20 g of commercially available titanium(IV) oxide 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 30 min. 24 g of 10 % strength sodium hydroxide solution were then added dropwise in the course of 30 min and the mixture was stirred for 30 min. A
25 further 12 g of 10 % strength sodium hydroxide solution were subsequently added dropwise in the course of 15 min and the reaction mixture was heated to 65°C and kept at this temperature for 1 h. After cooling, the suspension was filtered and the solid was washed 5 times with 50 ml of water. The moist solid was dried at 120°C in a vacuum drying cabinet for 4 h and then calcined at 300°C in a stream of air, a
30 ruthenium oxide catalyst supported on titanium(IV) oxide being obtained. The calculated amount of ruthenium was $\text{Ru}/(\text{RuO}_2 + \text{TiO}_2) = 4.7 \text{ wt.}\%$.

Example 3 (reference): Blank experiment with tin dioxide

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

Use of the catalysts in the oxidation of HCl

A gas mixture of 80 ml/min (STP) of hydrogen chloride and 80 ml/min (STP) of oxygen flowed through the catalysts from the example, the comparison example and the reference example in a packed fixed bed in a quartz reaction tube (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.

Table 1: Activity in the oxidation of HCl

Example	Composition	Chlorine formation	Chlorine formation
		mmol/min.g (cat)	mmol/min.g (Ru)
1	RuO ₂ /SnO ₂ (4.7 % Ru)	0.48	10.3
2 (comp.)	RuO ₂ /TiO ₂ (4.7 % Ru)	0.38	8.1
3 (ref.)	SnO ₂	(0.08)	-

Patent claims:

1. 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 oxygen-containing ruthenium compound.
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2. Process according to claim 1, wherein the catalyst is obtainable by a process which comprises the application of an aqueous solution or suspension of at least one halide-containing ruthenium compound to tin dioxide and the alkaline precipitation of the oxygen-containing ruthenium compound.
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3. Process according to claim 2, wherein an aqueous solution of RuCl_3 is used.
4. Process according to one of claims 1 to 3, wherein the reaction temperature during the catalytic gas phase oxidation is up to 450°C .
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5. Process according to one of claims 1 to 4, wherein the tin dioxide is present in the rutile form.
- 20 6. Catalyst for gas phase oxidations based on tin dioxide as support material and an oxygen-containing ruthenium compound.