PATENT SPECIFICATION

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COMPLETE SPECIFICATION

NO DRAWINGS

Improvements in the Removal of Impurities from Gases or Vapours

We, BADISCHE ANILIN- & SODA-FABRIK AKTIENGESELLSCHAFT, a German Joint Stock Company, of Ludwigshafen/Rhein, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the removal of impurities from gases or vapours in particular by treatment with copper compounds which have been precipitated together with one or more compounds of magnesium and/or iron, and, if desired, cobalt and/or nickel or which have been precipitated onto one or more precipitated compounds of these metals.

Impurities which can be removed in this way are for example one or more of the following: inorganic or organic sulphur compounds, oxygen, formaldehyde, acetylene and its homologues, halogens and their compounds such as hydrodgen chloride and vinyl chloride, hydrogen cyanide, pyridine, nitrogen dioxide, nitric acid, carbon monoxide, metal carbonyls and ammonia.

As gases or vapours which can be purified according to this invention there come into question for example nitrogen, carbon dioxide, ethylene or other gaseous saturated or unsaturated hydrocarbons or their derivatives, hydrogen or synthesis gases or cracking gases containing hydrogen, for example in conjunction with nitrogen or carbon monoxide. Hydrocarbons which are liquid at room temperature, such as gasoline or benzene, can also be purified in vapour phase according to this invention.

Suitable metal compounds are for example the hydroxides, carbonates and silicates of the said metals. Thus for example magnesium silicate and a copper compound may be precipitated together, or a copper compound may be precipitated onto precipitated magnesium silicate. In many cases it is preferable to subject the mass, after washing and drying, to a thorough kneading with not too large an amount of alkali silicate solution, and then to dry it again as far as possible at not too high a temperature and to shape it. The addition of too large an amount of alkali silicate may in some cases lead to undesirable side reactions and for this reason it is often preferable to carry out a short treatment with dilute waterglass solution only after the catalysts have been shaped. Other substances containing silicic acid may also be added.

Depending on the purpose for which the said mixture of metal compounds is to be used, it is recommendable, in order to increase the activity, to incorporate small amounts of compounds of the alkaline earth metals, zinc, cadmium, chromium, molybdenum, tungsten, vanadium, uranium, titanium and thorium singly or in admixture with one another, before or also after the precipitation. As compared with compounds previously known in the art in which the copper is precipitated on solid inactive carriers, the mixtures of metal compounds in accordance with the present invention have the special advantage that it is possible therewith to increase the copper content considerably.

The weight ratio of copper to the other metals may vary between about 1:20 and about 20:1. Advantageously it lies between 1:2 and 2:1.

The precipitations may be carried out at room temperature while stirring; raised temperature is not usually attended by any disadvantage. Commercial products may serve as initial materials. A heating of the washed, dried and broken or shaped mass to elevated temperatures before use is advantageous in some cases; the resistance to attrition can thereby be increased and a subsequent shrinkage avoided.

The precipitated masses may also be used on carriers, it being recommendable to choose those which already contain one component in the necessary amount, for example the substances arising from the production of aluminium, containing for instance 50% Fe_2O_3, 24% Ae_2O_3, 3% SiO_2, 8% TiO_2, 3% CaO, 4% Na_2O.

To increase the activity, the copper-containing mixture obtained by precipitation is preferably reduced. This can be carried out with hydrogen at temperatures of 80°C or advantageously higher, as for example 150°C. Instead of hydrogen there may also be used carbon monoxide, illuminating gas, producer gas, ethylene, industrial propane or other reducing substances. Substances, such as methanol, which decompose at high temperatures into carbon monoxide and hydrogen, may also serve as reducing agents. The temperature should be adapted to the substance used. Thus when using methanol a temperature of about 180°C is required, and when using ethylene or propane a temperature of about 280°C. The removal of acetylene from ethylene at 100°C or more may also be carried out without previous reduction.

The purification of the gases or vapours can be carried out at any pressure or reduced pressure at room temperature or even at temperatures below 0°C. In many cases it is advantageous to raise the temperature. Even when there is a high oxygen content in the gas, for example as in the case of air, it is possible without supplying heat to remove the oxygen down to a few thousandths% with a loading of 1 litre of copper-containing mass with 600 litres of air per hour. The heat occurring when the air is led over the reduced mass can be utilised for the regeneration of the exhausted masses, which is preferably carried out at about 150°C, so that the heat comsumption is relatively small.

The process may also be used for removing very small amounts of oxygen from gases. Thus the oxygen content of nitrogen can be reduced from 0.007% to 0.001% at room temperature and a loading of 5500 litres of gas per litre of copper-containing mass per hour. With a smaller loading, the oxygen is removed so completely that it can no longer be detected by the methods hitherto usual.

If it is desired to remove oxygen from hydrogen, it is preferable to work at a temperature which is considerably below the reduction temperature, i.e. at about 20°C.

Hydrogen may be purified also catalytcally from oxygen at 30°C and higher temperatures with the active masses according to this invention. Sulphur compounds, for example hydrogen, sulphide, carbon oxysulphide and thiophene, can also be removed even at room temperature to such an extent that they can no longer be detected analytically.

The removal of oxygen in addition to acetylene from industrial ethylene takes place even at room temperature. With a loading of 400 litres of gas per litre of copper-containing mass per hour, the oxygen content of ethylene can be reduced from 0.09% to 0.002% and the acetylene completely removed. Other impurities, such as hydrogen sulphide and traces of carbon monoxide, are also removed simultaneously. In this case it is preferable to work at about 100° C or higher.

The exhausted copper-containing mass can readily be reactivated by treatment with a reducing gas at about 150°C. A mass which no longer completely removes acetylene can be made serviceable again by leading nitrogen over it. Masses which contain unreduced copper compounds as effective components, when exhausted can be regenerated by leading air over them at 100°C or at higher temperatures.

In many cases it is advantageous to interpose a treatment with air before the treatment with reducing gases.

The following Examples will further illustrate this invention but the invention is not restricted to these Examples. The parts specified are parts by weight.

Example 1

88 ccs of a washed and shaped precipitate of basic copper carbonate on precipitated magnesium silicate (Cu-content about 26% by weight) are treated at 130°C with hydrogen until the colour has become uniformly brownish black. By leading 6 litres of air per hour over the thus pretreated mass at room temperature, the oxygen can be removed down to about 0.002% with rise in temperature.

By working under the same conditions with a commercial copper-chromium-silica gel catalyst, no reaction at all takes place. It is only at temperatures above 110°C that this catalyst begins to have a moderate action.

Example 2

Aqueous solutions of 128 parts of magnesium nitrate and 97 parts of potassium silicate are brought together while stirring, whereupon to the freshly precipitated magnesium silicate there is added an aqueous solution of 141 parts of copper nitrate, 2.6 parts of barium nitrate, 2.2 parts of zinc nitrate and 6.3 parts of chromium nitrate shortly after its union with a solution of 78 parts of sodium carbonate in 1000 parts of water. After washing and filtering off by suction, the product is made into a paste with

15 parts of 25% commercial waterglass solution, predried, shaped, dried at 60°C and reduced with hydrogen at 130°C.

Over the said mass there is led a technical ethylene which contains about 0.09% of oxygen, 0.11% of acetylene and traces of hydrogen sulphide, at 100°C and a loading of 400 litres of ethylene per litre of mass per hour. The gas is freed practically completely from the said impurities. The used mass is reactiviated by treatment with hydrogen or carbon monoxide at 136°C.

Propylene can also be purified in the same way. If the same mass is used to purify ethylene which contains only quite small amounts of impurities, room temperature is sufficient.

Example 3

Carbon dioxide containing 1% by volume of hydrogen sulphide is led at room temperature over a copper-magnesium silicate mass as described in Example 2 without the mass having been previously reduced. With a loading of the mass of 200 litres per litre of mass per hour, a gas is obtained in which hydrogen sulphide is no longer detectable.

Example 4

A mass is prepared from 300 parts of technical ferrous sulphate and 150 parts of copper sulphate by precipitation with 148 parts of sodium hydroxide, washed and dried. Then a stream of hydrogen containing 0.02% by volume of oxygen is led over the mass with an hourly loading of 900 litres per litre of mass, first for about 6 hours at 75°C and then at 50°C. The oxygen content falls to less than 0.002% with the formation of water.

If a mass is used which has been obtained by precipitation of 60 parts of copper hydroxide on 79 parts of a waste mass from the production of aluminium, which contains 36% of Fe_2O_3 and 31% of Al_2O_3, there is obtained under otherwise identical conditions so far-reaching a purification of the hydrogen that oxygen can no longer be detected therein by known methods.

Example 5

A mixture of the hydroxides of copper, iron and nickel which contains the metals in the ratio 1.4:1:0.6 and which has been obtained by precipitation, is washed, dried at 200°C, granulated and then reduced with hydrogen at 140°C. If a current of air be led without external supply of heat over this mass with a loading of 600 litres per litre of mass per hour, the oxygen content is reduced to 0.002% by volume. The nickel may also be replaced by cobalt. A mixture which has been obtained by precipitation from 150 parts of copper nitrate, 300 parts of iron nitrate and 440 parts of waterglass with 94 parts of sodium hydroxide behaves just as well.

Example 6

A purifying mass prepared according to Example 2, heated to 300°C and then reduced at 136°C completely removes about 25 micrograms of organic sulphur per cubic metre from hydrogen which is led thereover at room temperature and under a pressure of 220 atmospheres with a loading of 15,000 to 16,500 litres (decompressed) per litres per hour, for months at a time.

Example 7

0.6 kilogram of benzene having a thiophene content of 2.2 milligrams per 100 grams and 1,000 litres of hydrogen are led at 130°C and 100 atmospheres over the mass prepared according to Example 2 per litre per hour. The thiophene content of the benzene is reduced to 0.1 milligram per 100 grams.

WHAT WE CLAIM IS:—

1. A process for the removal of impurities from gases or vapours wherein the gas or vapour to be purified is led over a copper compound which has been precipitated together with one or more compounds of magnesium and/or iron, and if desired cobalt and/or nickel, or which has been precipitated onto one or more precipitated compounds of the said metals.

2. A process as claimed in claim 1 wherein the precipitated metal compounds are used on carriers.

3. A process as claimed in claim 1 or 2 wherein the precipitated metal compounds are reduced before use.

4. The process for the removal of impurities from gases or vapours substantially as described in any of the foregoing Examples.

5. Gases or vapours when purified by the process claimed in any of claims 1 to 4

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