Visualization of the absorption of UV light by titanium dioxide

Material

Plastic box with lid, thermal imaging camera for smartphone, smartphone, UV flashlight, stand and clamps

Chemicals

Titanium dioxide (Evonik P25)

Set-up

Experimental procedure

Step 1 Using a stand, the UV flashlight is pointed at the titanium dioxide powder through one hole in the plastic box. To put the thermal imaging camera into place, the flashlight is turned on and the light is then directed under the second hole for the thermal imaging camera.

Step 2 Next, the thermal imaging camera is inserted into the smartphone and the app is opened. If necessary, the camera can be calibrated using a beaker of cold water. In order to do so the thermal camera is pointed at the surface of the water until the image in the app turns blue.

Step 3 Afterwards the camera is positioned in the second hole of the plastic box. The titanium dioxide powder is then irradiated for 5 min and the observations recorded on the thermal imaging camera. Repeat the procedure with white light and other colours of light.

Tasks

T.1.1 Describe what kind of light is absorbed by titanium dioxide and which kind of light the sensor of the thermal imaging camera can detect.

T.1.2 Consult a spectrum of electromagnetic radiation and find out about the relation between wavelength and energy as well about the parts of UV-, VIS- and IR-radiation within the spectrum. Complete the following sentence:

"In the experiment high energy __________________ light is

converted into low energy _________________ light."

T.1.3 If there is no titanium dioxide in the box, the thermal imaging camera does not detect any irradiation when the UV light is pointed at the bottom of the box. Explain the function of titanium dioxide in this experiment.

Is titanium dioxide carcinogenic or not?

Info Since 2016, the ECHA (European Health Agency) has been discussing the classification of titanium dioxide as a carcinogenic hazardous substance. Titanium dioxide is used as a white pigment due to its opacity in products such as paint, lacquers or plastics. But also in food as well as cosmetics the white pigment was used for coloring. A number of institutions have commented in detail on the potentially hazardous nature of titanium dioxide.

T.2 Read the following text excerpts of selected statements M1-M3 and summarize the central statements of the authors.

M1 „These claims misrepresent the conclusions of the European Food Safety Authority (EFSA) in its 2021 opinion. EFSA did not conclude that titanium dioxide is genotoxic or causes harm to humans. EFSA only concluded that there was uncertainty regarding potential genotoxicity that required further investigation, a conclusion that other global regulators have disagreed with.“

M2 „The Court of Justice of the European Union has ruled to annul the European Commission's 2019 classification of titanium dioxide (...) as a carcinogen. The court questioned the reliability and acceptability of the study on which the Commission's classification was based, and decided that the classification and labeling of titanium dioxide as carcinogenic is not valid as the substance is not intrinsically cancer-causing.“

M3 „The safety of the food our citizens eat and their health are non-negotiable. This is why we ensure strict and continuous scrutiny of the highest safety standards for consumers. A cornerstone of this work is to make sure that only safe substances, backed by sound scientific evidence, reach our plates. With today's ban, we are removing a food additive that is no longer considered as safe. I count on Member States authorities for their cooperation in ensuring that food operators end the use of E171 in foods.“

T.3 Research the sources from which the text excerpts M1 - M3 are taken and assign the author, addressee, and the context in which the articles can be found to each of them.

T.4 Using the following information, evaluate the classification of titanium dioxide as a hazardous substance.

Info

In November 2022, the General Court of the European Union ruled that the classification of titanium dioxide as a carcinogen by inhalation is not lawful. The reason given was that the European Chemicals Agency (ECHA) had drawn incorrect conclusions from the available data. The EU Commission had followed ECHA's recommendation and thus made the same mistake in classifying titanium dioxide as a probable carcinogen. The EU's classification applied only if titanium dioxide was present as a powder, with at least 1% of the particles having a diameter of ≤10 μm. Titanium dioxide had therefore not been banned, but had to be labeled. However, since this classification applies only to a specific form (powder), it is not an intrinsic property of titanium dioxide itself. This means that titanium dioxide does not always have a carcinogenic effect, but only under the conditions mentioned above. Therefore, the General Court of the European Union has ruled that the classification must be revoked, since titanium dioxide does not itself have a carcinogenic effect. From the judgment unaffected is the ban on titanium dioxide as a food additive E 171 since summer 2022.

See: https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX%3A62020TJ0279

T.5 Discuss which aspects must be taken into account in order to evaluate a statement made by an information source.

T.6 A friend sends you a voice message saying that he has only sunscreen with titanium dioxide at home and is worried about using it. He tells you that he would rather go outside without any sun protection than using this sunscreen. Write a text message to your friend and give him advice on how to act.

Photocatalytic degradation of air pollutants

Material

80 mL round-bottomed flask, 3 UV flashlights, stand and clamps, Parafilm®, glass wool, rubber tubing, 100 mL infusion bag, 5 25 mL glass vials with lid, Luer taper: 2-way stopcock, 3-way stopcock, 5 Luer lock connections, 2 60 mL syringes with 2-way stopcock

Chemicals

Titanium dioxide (Evonik P25), 15 g copper powder, 5 mL concentrated nitric acid, Griess test reagent or nitrite test strips

Set-up

Experimental procedure I - Preparation of the nitrous gases

Step 1 Prepare the set-up as above and additionally seal all connections with Parafilm®. From left to right: 80 mL round-bottomed flask with a two-way stopcock and an attachment with side extension with glass wool, connecting tube, three-way stopcock with infusion bag and disposable syringe connected to a two-way stopcock.

Step 2 Add enough copper powder to the round-bottomed flask so that the bottom is completely covered. Dilute 5 mL of concentrated nitric acid in a ratio of 1:5 and add it to the copper in the round-bottomed flask. The ratio is sufficient to produce nitrogen oxides (nitrous fumes) for one run.

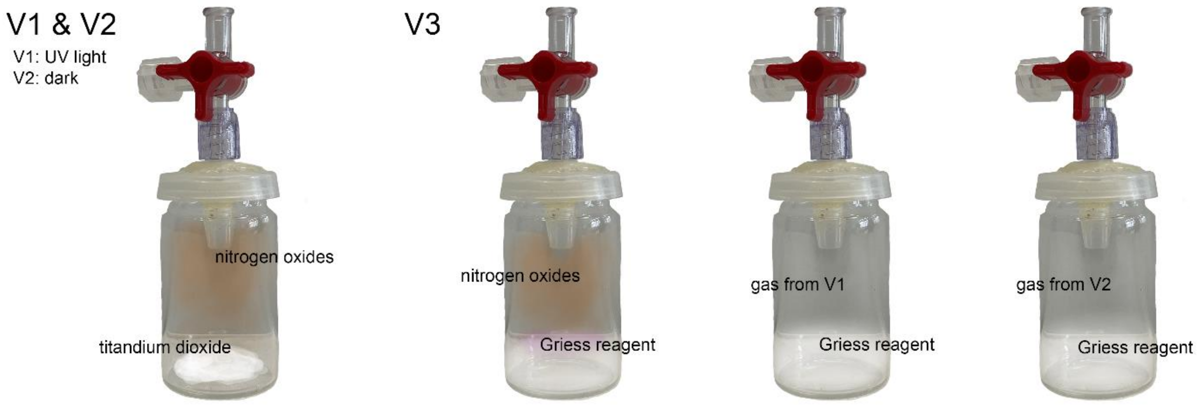
Experimental procedure II

Step 3 Add a layer of titanium dioxide powder in two of the prepared glass vials.

Step 4 Point UV-light with 3 flashlights at one of the glass vials and fill it with nitrogen oxides (approximately 50 mL) via the three-way stopcock using the syringe (V1). Also fill the other glass vial with nitrogen oxides and place it in the dark (V2). Make sure both lids are closely sealed with Parafilm® during the irradiation. Leave both samples for 20 min.

Step 5 In the meantime, prepare three glass vials with the Griess reagent for detection. For the reference sample, transfer nitrogen oxides from the gas evolution set-up to one of the three glass vials (V3).

Step 6 After the irradiation time has passed, remove the gas from V1 and V2 using a new syringe and transfer each gas sample to one of the remaining glass vials with the Griess test from *Step 5*.



Tasks

Info The main sources of nitrogen oxides are combustion engines and furnaces. The nitrogen oxides released into the environment via exhaust gases damage the health of humans, animals and vegetation in many ways. The reason is the strong oxidizing effect of nitrogen dioxide. Furthermore, as precursors, they contribute to the formation of ground-level ozone and secondary particulate matter. They also have an over-fertilizing and acidifying effect in the environment, so that they damage plants and pollute water and soil.

T.1.1 Using the gas evolution set-up, you have produced nitrogen oxides, primarily nitrogen dioxide. Write a reaction equation for the reaction and state how the evolving nitrogen dioxide can be identified.

T.1.2 Nitrogen oxides can be detected via the Griess test. The intensity of the observed color can also be used to estimate the concentration. Describe and compare the observations from the experiment.

Info Photocatalysts catalyze a reaction when exposed to light of a suitable wavelength. Semiconductors, such as titanium dioxide in this experiment, are used as photocatalysts. Titanium dioxide which is irradiated by UV light can degrade nitrogen oxides. In this process, a photoredox reaction takes place. This is why titanium dioxide is also used in photocatalytic wall paint, which is intended to reduce nitrogen oxide pollution in cities.

T.1.3 Add oxidation numbers to the simplified reaction equation for the degradation of nitrogen oxides and set up the partial reactions (oxidation and reduction).

$$O_2\ (g) + NO_2\ (g) + NO\ (g) + H_2O\ (l) \xrightarrow{TiO_2} HNO_3\ (aq)$$

T.1.4 Based on your observations and the information provided, explain the function of the titanium dioxide in this experiment.

Wall paint as a sustainable solution against air pollution?

Info For the use as photocatalyst titanium dioxide is used in the form of nanoparticles. Nanoparticles are particles that have a size of 1 to 100 nm. The titanium dioxide from Evonik (P25), the average size of a particle is <21 nm. Nanoparticles have special chemical and physical properties that differ from those of larger particles. Such properties can be, for example, a higher chemical reactivity due to the increased surface area in relation to the volume or the increasing influence of surface forces such as Van der Waals forces. Therefore, nanoparticles have numerous potential uses in research and applications. However, due to their small size, risks of nanoparticles are also discussed due to contact or entry into the environment.

T.2 Research what potential harmful effects of nanoparticles are currently being discussed and summarize your findings.

T.3 Photocatalytic degradation of nitrogen oxides produces nitric acid, which instantly dissolves when in contact with atmospheric moisture. Thus, dissolved oxonium ions and nitrate ions are present and pass into the groundwater. Using the keywords "acidification" and "eutrophication," explain possible consequences that can occur as a result of an increase in ion concentration in the environment. Possibly consult other sources of information for evaluation.

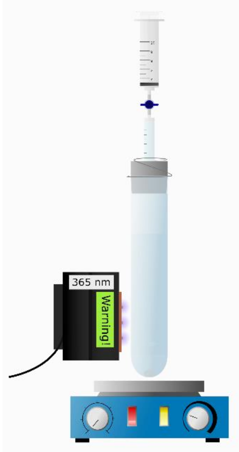
T.4 Discuss the extent to which the use of photocatalytic wall paint can be considered a sustainable solution to reduce the amount of nitrogen oxides. In doing so, suggest alternative ways to reduce them.

Photoreforming of ethanol

Material

Balance, ultrasonic bath (optional), large test-tube (quartz glass), beaker, magnetic stirring plate with stirring fish (small form), one-hole rubber stopper, 10-mL syringe, 1-mL syringe, cannula, two-way stopcock, stand & clamps, high-power LEDs (365 nm), gas bag with septum, Petri dish, lighter

Set-up



Chemicals

ethanol-solution (10 Vol.-%), TiO_2/Pt-catalyst, soap solution

Experimental procedure I - Production of hydrogen gas

Step 1 Carry out the experiment step by step according to the instructions below. Irradiate the suspension for at least 30 minutes.

Put 50 mg of the TiO_2/Pt-catalyst in a large test-tube.

Add the ethanol solution (10 Vol.-%) to the catalyst and fill the test-tube to about 2 cm below the rim.

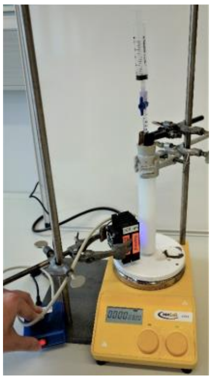
Put the suspension into an ultrasonic bath for 3 minutes (optional step).

Add a stirring fish to the suspension.

Close the test-tube with a one-hole rubber stopper with an inserted 1-mL syringe and attached two-way stopcock.

Clamp the test tube with attachment to a stand above a magnetic stirring plate. Place a 10-mL syringe on top of the two-way stop-cock. The plunger of the syringe should be pressed down.

Fix another clamp directly on top of the stopper so that it is firmly placed on the test-tube.



Switch on the magnetic stirring plate (min. 300 rpm) and the high-power LEDs (365 nm) to irradiate the suspension (min. 30 min).

Experimental procedure II - Examination of the gas sample

Step 2 Close the two-way stopcock after irradiation. Now remove the 10-mL syringe with the two-way stopcock from the 1-mL syringe and place a cannula on the two-way stopcock.

Note the amount of produced *gas* and calculate the amount of oxygen gas needed to perform a complete oxyhydrogen test (Note: Assume the gas sample is pure hydrogen in your calculation)

_______ mL produced gas

Volume of oxygen needed for a oxyhydrogen test: _______ mL oxygen gas

Step 3 Take the calculated amount of oxygen gas from the gas bag. To do this, insert the cannula into the septum connected to the gas bag. Open the two-way stopcock and suck the required amount of oxygen into the syringe to mix with the gas.

Step 4 Fill a Petri-dish with about 0.5 cm of soap solution. Hold the tip of the cannula into the soap solution and form a gas bubble of about 0.5 mL (Fig. 1). Ignite the gas bubble using a lighter.

Figure 1: Injection of gas mixture into a soap solution

Tasks

Info **Gas chromatography (GC)**

Gas chromatography is an analytical method for analysing the composition of unknown gas samples. A gas sample is injected into a column. A carrier gas (e.g. nitrogen) is passed through the column and transports the gas sample. Depending on the components of the gas sample, these remain in the column for different periods of time, as they interact to varying degrees with the material the column is made of. At the end of the column, a detector can be used to determine how long it takes the components of a gas sample to pass through the column. If samples of unknown gases are injected, too, the resulting chromatograms can be compared with those of the unknown gas sample. The chromatograms can then be evaluated graphically. The size of the areas below the graphs can be used to determine the amount of gas components in a known sample.

T.1 Fig. 1 shows two gas chromatograms. Both pure hydrogen gas (reference sample) and a gas sample taken after irradiation were analysed. Using the values given, calculate what proportion of hydrogen is present in the gas sample.

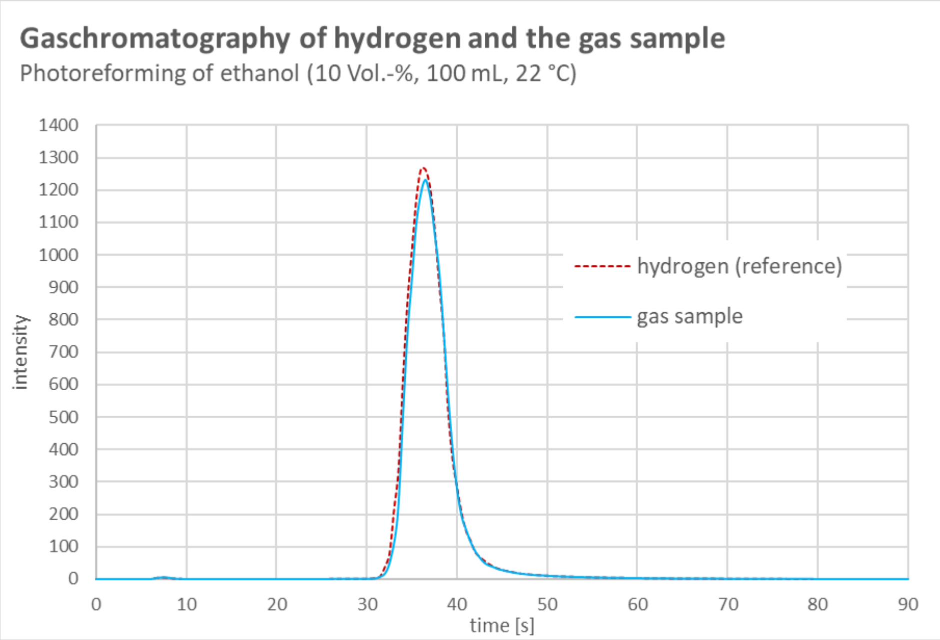


Figure 1: Diagram of the GC examination of the gas sample and the GC examination of hydrogen gas (reference sample).
The area (A) below the red graph is *6655,68 A*.
The area (A) below the blue graph is *6319,99 A*.

Additional task: The role of the catalyst

T.1* Follow the link: https://chemiedidaktik.uni-wuppertal.de/fileadmin/Chemie/chemiedidaktik/files/html5_animations/cbl_group/photocatalysis/photocatalysis.html or the QR code shown.
Explore the animation and describe in a few sentences the role of the photocatalyst. Assign the following particles to the donor particles (D/$D^{+}\cdot$) and acceptor particles (A/$A^{-}\cdot$) for the process of photoreforming of ethanol:

H^+, H_2, CH_3CH_2OH, CH_3CHO

Info **Hydrogen and green energy**

For several years now, the use of hydrogen has increasingly been the subject of political and social discussions in the context of the turn from fossil fuels to renewable energy sources and the reduction of CO_2-emissions. In addition to the transport sector, especially the steel industry is seen as having great potential for the use of hydrogen. But what are the advantages or disadvantages of the increased use of hydrogen? And which production routes can meet the requirements of environmental protection, society and industry?

T.2 Using M1, compare green and grey hydrogen in a table. Also note the advantages and disadvantages of producing hydrogen by steam reforming.

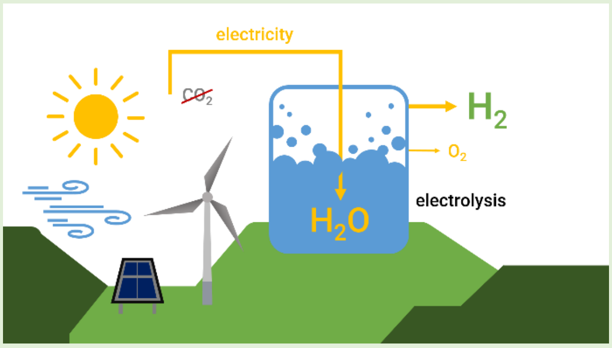
T.3 Work in pairs. One reads interview excerpt M2, the other reads interview excerpt M3. Discuss the statement that hydrogen obtained via steam reforming can be seen as the basis for a sustainable energy transition.

T.4 In small groups, find arguments for the use of green hydrogen. Formulate proposals that you would address to political representatives regarding the conditions under which hydrogen can be used as an energy carrier of the future. Also consider different positions from the economy, environment and society.

M1

Green Hydrogen

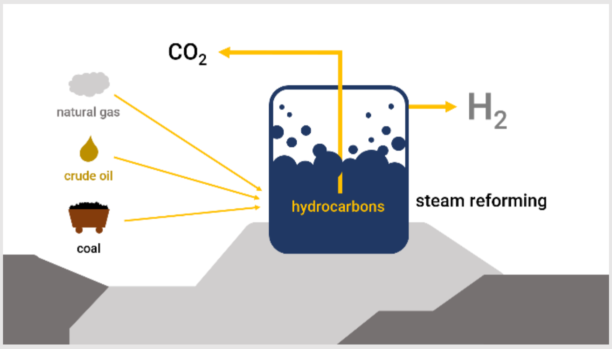
Green hydrogen is classified as carbon-neutral. This hydrogen gas is mostly obtained by electrolysis of water. However, the important factor in this industrial production route is that the electricity for electrolysis is generated from renewable energies such as solar or wind energy. Green hydrogen includes also the production of hydrogen by fermenting biomass and using it for microbial fuel cells. Photoreforming is also a way to produce green hydrogen. It can be performed at room temperature or slightly elevated temperatures (approx. 60 °C) and ambient pressure. The efficiency of this process is depends on the substances used (methanol > ethanol > glucose > sucrose > starch > cellulose). However, none of these production routes is yet widely used in industry.



Picture adapted from: https://www.enbw.com/unternehmen/eco-journal/wasserstoff-farben.html

Grey Hydrogen

Steam reforming of fossil fuels (natural gas, crude oil, coal) is currently used to produce a large amount of industrially produced hydrogen. It is carried out with a catalyst at high pressure (15 - 25 bar) and high temperatures (750 °C - 1000 °C). It is an endothermic reaction, so the required amount of heat must be supplied. The overall efficiency of steam reforming is 60-70 % of the calorific value of natural gas. This means that 60-70 % of the chemical energy stored in natural gas is stored in the hydrogen produced. The remaining 30-40 % are lost in the conversion process. This production way is referred to as grey hydrogen and is associated with a high amount of carbon-emissions into the environment.



Picture adapted from: https://www.enbw.com/unternehmen/eco-journal/wasserstoff-farben.html

M2 ***High time to lead German industry to hydrogen***

Translation of an interview with Dr. Timm Kehler, Executive Board, Zukunft Gas e.V.* 31.01.2022

* Zukunft Gas e.V. is a lobby organization. It represents the interests of companies in the German gas industry and promotes the public image of natural gas as an energy source.

[…] A key role for rapid climate protection is played by industry, which produces the second-largest share of greenhouse gas emissions in Germany. One of the main reasons is the high energy demand, as shown by the steel industry, for example: Not only is it responsible for a large share of hard coal consumption, it also represents the largest market segment of the German gas market, accounting for around 35 percent of total sales. This makes industry the perfect place to use hydrogen. Gas is the most important energy source in German industry, ahead of electricity, and is used there mainly for three reasons:

Gas is used to generate process heat and is used in various production processes that require steam, hot water, heat or cold. This accounts for more than two-thirds of industrial gas sales.

However, industry also uses gas to generate electricity. In power plants close to production sites, the industry converts 20 percent of the natural gas it uses into electricity. [...] Overall, the industry generated around 53 TWh of electricity in 2019, half of which was from natural gas. It is true that more renewable energies will also be used here. However, many industrial processes rely on a constant flow of electricity, which wind and sun cannot guarantee due to weather conditions. Power outages due to dark periods also cause considerable economic losses that would be unsustainable in the long term. [...]

Finally, the industry uses natural gas as a basic material, primarily to produce ammonia, hydrogen or methanol. This material use accounts for 11 percent of natural gas sales. [...]

The CO_2-free gas hydrogen is at the same time the central element for further decarbonizing the industry in the future. One day it will be used instead of fossil fuels. One example of possible applications is the production of green steel. Germany produces around 45 million tons of steel annually [...], mostly with high coal consumption in blast furnaces. If these were converted to hydrogen, about 43 million tons of CO_2 could be saved per year.

[...] In order to provide sufficient quantities of affordable hydrogen for the industry, especially in the start-up and transition phase, it will be necessary to continue producing the hydrogen to be used on the basis of natural gas. This is because hydrogen from renewable sources will continue to be scarce and comparatively expensive for a long time to come. The resulting cost pressure threatens to cause energy-intensive processes to migrate abroad. This would not only lead to a considerable detriment of Germany as a business location, but would also be tantamount to a massive step backward for climate protection. This is because, on the one hand, other countries usually have much less stringent emission requirements, but on the other hand, Germany must also prove that its model for the energy turnaround is competitive and can therefore also serve as an international role model.

[...] The large-scale use of hydrogen is indispensable for a green industry and a climate-neutral Europe. Natural gas paves the way for this in a climate-friendly way, provides the basis for an affordable transformation and helps to quickly save large quantities of emissions. Making hydrogen the energy of the future? It's possible with gas!

Source: Handelsblatt, https://live.handelsblatt.com/hoechste-zeit-die-deutsche-industrie-zum-wasserstoff-zu-fuehren/ (20.05.2023).

M3 Interview: "Energy sources of the future" in the Federal Network Agency Insight Blog

Interviewed persons:
Eva Haupt, Frauke Horstmann and Andreas Müller are members of the Federal Network Agency

Q: There are different types of hydrogen. Which one does the German government want to promote according to its National Hydrogen Strategy?

Andreas Müller: "What is understood by hydrogen in the current discussion, and what benefits us most in terms of the climate, is green hydrogen. This is produced by electrolysis of water with the help of electricity from renewable energies - this can only happen in some parts of Germany. We would need a lot of renewable energies for this. In perspective, we have to rely on being able to buy the hydrogen abroad - just as we do now with oil or gas."

Q: Which kind of hydrogen is currently mostly consumed in Germany? Green?

Frauke Horstmann: "No. On the one hand, hydrogen is used that is produced as a by-product from chemical processes. On the other hand, hydrogen obtained by means of steam reforming is used. This is done with the help of natural gas, and the resulting CO_2 is not injected into the ground in Germany today - but released."

Eva Haupt: "In the long run, producing hydrogen from natural gas is not a solution. What could happen is that we now set up a hydrogen economy and infrastructure and the industry simply produces hydrogen from steam reforming - and thus releases the CO_2 into the atmosphere. That would be the worst case scenario and would not serve the goal of the desired CO_2 reduction. The only thing that will help is a certification system that prevents exactly this effect and enables green hydrogen, which is unfortunately currently much more expensive than that produced from steam reforming, to have priority."

Andreas Müller: "In this regard, one must of course see that hydrogen is generally expensive and is unlikely to become cheap in the foreseeable future. Whereas natural gas is a very cheap commodity. That's why hydrogen will have a hard time at the beginning if you don't support it in a targeted way. The German government plans to invest 7 billion euros in hydrogen technologies and the market ramp-up in Germany. 700 million of that for infrastructure projects."

Source: Federal Network Agency, https://www.bundesnetzagentur.de/DE/Allgemeines/DieBundesnetzagentur/Insight/Texte/Energiewende/Blog6_Energiewende_Wasserstoff.html (20.05.2023).