

Carbon Dioxide-Free Hydrogen Production with Integrated Hydrogen Separation and Storage

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An integration of CO₂-free hydrogen generation through methane decomposition coupled with hydrogen/methane separation and chemical hydrogen storage through liquid organic hydrogen carrier (LOHC) systems is demonstrated. A potential, very interesting application is the upgrading of stranded gas, for example, gas from a remote gas field or associated gas from off-shore oil drilling. Stranded gas can be effectively converted in a catalytic process by methane decomposition into solid carbon and a hydrogen/methane mixture that can be directly fed to a hydrogenation unit to load a LOHC with hydrogen. This allows for a straight-forward separation of hydrogen from CH₄ and conversion of hydrogen to a hydrogen-rich LOHC material. Both, the hydrogen-rich LOHC material and the generated carbon on metal can easily be transported to destinations of further industrial use by established transport systems, like ships or trucks.

Introduction

Today, more than 60 million tons of hydrogen are produced and utilized industrially.^[1] The largest part of this quantity is applied in the petrochemical and chemical industry, mainly for desulphurization of fuels and hydrogenation reactions, for example, the production of ammonia and methanol.^[2] In the near future, hydrogen is expected to gain additional importance as a green energy vector for the mobility sector, because its combustion in fuel cells or combustion engines produces water as the only combustion product.^[3,4]

However, to consider hydrogen as a sustainable fuel, it is important to assure that its production is free of CO₂ emissions. This is not a trivial task given that 95% of today's industrial hydrogen production is generated from fossil fuels by steam reforming, partial oxidation, or gasification processes. All of these produce significant amounts of CO₂. For example, 1 ton of hydrogen produced by using methane as raw material was reported to produce more than 10 tons of CO₂ simply owing

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to the stoichiometry of the methane reforming and water-gas shift reactions, the energy consumption of the process, and the molecular masses of the molecules involved.^[5]

Aiming for the sustainable (zero emission) production of hydrogen, electrolysis of water using renewables is one possible option. However, electrolysis is still relatively expensive (3 \in per kg of hydrogen).^[6] As an alternative, hydrogen production from hydrocarbons avoiding CO₂ emissions can be considered. Whereas CO₂ capture and storage (CCS technology) is energy and cost intensive,^[7] and associated with ecological uncertainties, hydrogen production through catalytic decomposition of hydrocarbons linked to elemental carbon sequestration is a promising option. In particular, the moderately endothermic catalytic methane decomposition to carbon and hydrogen holds great promise for the sustainable production of hydrogen.^[8]

$$CH_4 \rightarrow C + 2H_2 \quad \Delta H_{25} \ ^{\circ}C = 74.5 \text{ kJ mol}^{-1} \tag{1}$$

Whereas purely thermal decomposition of methane occurs at process temperatures above 1200 °C,^[9] the use of an appropriate catalyst has been reported to bring the operating temperature down to 550 °C.^[10] Regarding suitable catalysts for catalytic methane decomposition (CMD), the literature pays special attention to supported group 8-10 base metal catalysts, in particular nickel, iron, and cobalt.[11] While nickel catalysts are limited in CMD to operating temperatures below 700 °C, iron systems have been reported to operate even above this temperature.^[11] Despite these differences, any catalyst used for CMD eventually deactivates as result of deposition of carbon-rich polyaromatic structures, amorphous, filamentous, or graphitic carbon on its surface.

CMD is a complex process that can be divided into three key steps: (i) hydrogen generation by a sequence of methane adsorption and dissociation at the metal surface and simulta-



neous desorption of hydrogen; (ii) formation of carbon nanomaterials by dissolution of chemisorbed carbon atoms into the metal followed by diffusion of carbon through the bulk of the metal where carbon atoms precipitate onto the support forming the nanostructure; and (iii) catalyst deactivation caused by slower and slower carbon diffusion through the metal particle and formation of graphitic carbon at the particle surface thus reducing the active surface area.^[12] Figure 1 illustrates these three steps.



Figure 1. Representation of hydrogen production, carbon nanomaterial (CNM) formation, and growth in the CMD process.

A significant part of the world's methane reserves is located far from industrial and population centers, and transportation cost hinders its efficient utilization. Moreover, many of these gas fields are far too small to justify chemical conversion of methane by current gas-to-liquid technologies that gain economic attractiveness only in the form of world-scale units.^[13]

Thus, the term "stranded gas" refers to methane resources at places and in quantities that do not justify the installation of pipeline infrastructures, for example, associated gas from an off-shore oil drilling rig or from oil drilling at remote locations in the desert. Currently, such stranded gas is typically flared, vented or re-injected.^[14] Consequently, new technologies able to convert this gas in small facilities of low investment cost directly at the gas source would benefit from a very low or even negative feedstock price. It is common understanding among experts that the amount of stranded gas is on the order 40 to 60% of the proven global natural gas resources.^[15]

CMD is, in principle, ideally suited for a treatment of stranded methane. Compared to common gas-to-liquid technology, CMD represents a relatively simple one-step process that converts methane directly into two valuable products, hydrogen and carbon-loaded metal. However, two aspects prevent the use of CMD as economic option in stranded gas upgrading: (i) for thermodynamic reasons, the CMD process provides no full methane conversion in the desired temperature range of its catalytic operation, and hydrogen-methane separation is required to recycle unconverted methane back into the CMD process and to obtain pure hydrogen; and (ii) whereas carbonloaded metal can be easily shipped from the remote place to a potential consumer, the produced hydrogen is characterized by an extremely low volumetric energy density (only 3 Wh L⁻¹ at ambient pressure), and its transport over long distances is unsuitable in elemental form. Even the transport of compressed gaseous hydrogen (CGH2, typically up to 700 bar \approx 79 MPa pressure) or liquefied cryogenic hydrogen (LH2, typically at -253 °C), would not solve the problem of an efficient transport of elemental hydrogen, as the volumetric storage density is still modest (see Table 1). Moreover, hydrogen compression and cooling come along with additional energy consumption and require special infrastructure, such as compressor stations, compressed gas tankers, or transport vehicles with cryogenic tank systems.

Table 1. Volumetric and gravimetric energy density of elemental hydrogen compared to fossil fuels. ^[16]					
Energy source	Energy carrier	Energy density [kWhL ⁻¹]	Energy density [kWh kg ⁻¹]		
Fossil fuels Hydrogen	Gasoline Diesel Heavy oil Natural gas H_2 (atm) GCH ₂ (700 bar) LH ₂ (liquid) LOHC (H18-DBT)	8.6 9.8 10.7 2.4 0.003 1.3 2.4 1.87	11.4 11.8 11.0 11.1 33.0 33.0 33.0 2.05		

In this contribution, we propose the combination of CMD with hydrogen storage in liquid organic hydrogen carrier (LOHC) systems as a very attractive option to overcome the named limitations and to establish a technology to upgrade stranded methane in the form of storable and transportable hydrogen equivalents ready for industrial use at any far distant location. LOHC systems are composed of pairs of hydrogenlean, mostly aromatic compounds and hydrogen-rich, mostly alicyclic compounds. By reversible hydrogenation and subsequent dehydrogenation, LOHCs can be used to safely bind, store, transport, and release hydrogen on demand.^[17-20] Depending on the LOHC system, hydrogen storage is possible at a material-based energy density of up to $72 g_{H_2} L_{LOHC}$ or 2.4 kWhL⁻¹. Thus, the concept allows hydrogen storage over long times at high volumetric energy densities as well as hydrogen transport over long distances without losses using existing infrastructure for liquid fuels (e.g., ships, trucks, rail trucks, and tank farms). Figure 2 shows the proposed combination of CMD and hydrogen storage through LOHC systems.

Herein, we demonstrate new insight into the combination of CMD and LOHC hydrogenation by using representative hydrogen-methane mixtures from CMD as substrate for charging a selected, suitable LOHC system.

Hydrogen production through CMD

The influence of the reaction temperature on hydrogen yield in CMD was studied using a 20 wt% Ni/Al₂O₃ catalyst in the temperature range of 550 to 700 °C. Figure 3 shows the outlet hydrogen stream as well as methane conversion as a function





Figure 2. The proposed two-step upgrading process for stranded gas: methane is converted in a catalytic decomposition process to carbon and hydrogen, which is subsequent purified from remaining methane and transferred into a transportable form by LOHC hydrogenation.



Figure 3. Effect of reaction temperature on the evolution of hydrogen from methane by CMD at a gas hourly space velocity (GHSV) of $12500 h^{-1}$; left axis (black symbols) shows the generated volumetric hydrogen flow; right axis (red symbols) shows the degree of methane conversion.

of reaction time. The nickel catalyst maintains its initial activity at a reaction temperature of 550 °C for the reaction time of 5 h producing a constant hydrogen outlet stream of $54\ mL_N min^{-1}g_{cat}^{-1}$ (where L_N refers to the volume at normal conditions: 1 bar, room temperature) corresponding to a methane conversion of 14%. A slight increase in reaction temperature of 50°C resulted in a hydrogen outlet stream of 92 mL_Nmin⁻¹g_{cat}⁻¹. However, the catalyst experienced slight deactivation at 600 °C during the reaction time of 5 h; therefore, a loss in methane conversion of around 5% was observed during this time. Further increase in reaction temperature resulted in an increase of the initial hydrogen yield to 122 mL_Nmin⁻¹ g_{cat}^{-1} at 700 °C. However, at this temperature the evolving hydrogen content dropped quickly until complete catalyst deactivation after approximately 1.5 h on stream.

The observed fast deactivation behavior of Ni/Al_2O_3 at 700 °C can be attributed to the formation of different carbon species during methane decomposition. TEM characterization of the spent catalyst gave us more insight into the morpholog-

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Figure 4. TEM micrographs of the spent Ni/Al_2O_3 catalyst at (a,b) 600 $^\circ C$ and at (c,d) 700 $^\circ C.$

ical differences of the deposited carbon as a function of different reaction temperatures. Figure 4a-d show some representative TEM micrographs of the spent catalyst at 600 (Figure 4a, b) and 700 °C (Figure 4 c, d). The TEM measurements reveal the presence of carbon material on the catalyst surface, which is mainly deposited in the form of nanostructures with varying morphology depending on the reaction temperature. Comparing the nanostructures formed at 600°C with those formed at 700 °C, the material obtained at 600 °C consists mainly of hollow cylindrical filaments emerging from the nickel particles (Figure 4a) coexisting with filaments containing a metal particle on their tip, which is uniformly coated with parallel planes of graphene (Figure 4b). An examination of the TEM measurements evidences that long filaments with no particle on their tip are more abundant than filaments with uniform coatings. In contrast, carbon material formed at a reaction temperature of 700 °C shows a less homogenous morphology distribution. Nanotubes with coated metal particles on their tip (Figure 4c), uniformly coated nickel particles referred to as nano-onions, as well as bamboo shaped filaments (Figure 4d) were obtained during this reaction. The results suggest, that high temperatures cause fast catalyst deactivation owing to the immediate formation of a graphitic layer encapsulating the catalytically active metal particle. In contrast, the catalyst maintains its activity owing to the generation of nanotubes at lower reaction temperatures.

Hydrogen separation and storage through LOHC hydrogenation

The LOHC hydrogen storage technology is based on reversible hydrogenation of double bonds. In the past, various compounds have been investigated for their suitability as LOHC systems ranging from small aromatics, for example, benzene/ cyclohexane^[21] and toluene/methylcyclohexane,^[22-26] to con-



densated aromatics (e.g., naphtaline/decalin^[27,28]) and N-containing aromatics [e.g., *N*-ethyl-carbazole(NEC)/dedecahydro-*N*-ethyl-carbazole^[29-33]]. All the named systems have their advantages and disadvantages regarding hydrogen capacity, hydrogenation enthalpy, thermal stability liquid range, toxicity, and technical availability.

An excellent tradeoff of all these highly relevant properties for suitable LOHC materials is found for the relatively recently reported system dibenzyltoluene (H0-DBT)/perhydrodibenzyltoluene (H18-DBT).^[34-36] Dibenzyltoluene is a commercial heat transfer oil (marketed under the tradenames Marlotherm SH© or Farolin WF0801©; price is below $4 \in kg^{-1}$ on ton-scale) with known and very favorable toxicology (non-toxic, non-mutagenic, non-carcinogenic, not labelled as hazardous good in transportation), high thermal stability, and excellent physico-chemical properties for many LOHC applications. The isomeric mixture of dibenzyltoluenes has a melting point of -34 °C and a boiling point of 390 °C.^[36] During hydrogenation, H0-DBT binds 6.2 wt% hydrogen corresponding to an energy content of 2.05 kWh kg⁻¹. Figure 5 shows a depiction of the H0-DBT/ H18-DBT hydrogen storage system.



Figure 5. Storage and transport of hydrogen by reversible catalytic hydrogenation/dehydrogenation of dibenzyltoluene/perhydro-dibenzyltoluene.

As shown by the recent studies of Brückner et al.,^[34] complete hydrogen release from H18-DBT is possible by a catalytic, endothermic dehydrogenation reaction, for example, in the presence of Pt on alumina catalysts. These studies could also show that dehydrogenation of H18-DBT proceeds under appropriate conditions (i.e., 310 °C, $1 \text{ bar} \approx 0.1 \text{ MPa}$) with negligible fragmentation of the hydrogen carrier molecule. This enables the utilization of the H0-DBT/H18-DBT LOHC system in repeated hydrogenation-dehydrogenation cycles. Due to these very favorable properties we will restrict ourselves in this publication to the catalytic hydrogenation of H0-DBT as most interesting way to purify and store hydrogen from the CMD process.

The hydrogenation of H0-DBT comprises the consecutive hydrogenation of three isolated phenyl rings. For a quantitative comparison, the degree of hydrogenation (DoH) is defined as the ratio of the bound hydrogen and the maximum hydrogen up-take capacity. For the experiments reported here dealing with the hydrogenation of H0-DBT with hydrogen/methane mixtures using a batch reactor, the DoH has been determined by mass flow measurements according to Equation (2) and independently by ¹H NMR spectroscopy.^[37]

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DoH (t) =
$$\frac{\int_{t_0}^{t} n_{H_2,\text{reaction}}(t) dt}{n_{H_2,\text{max}}} = \frac{\int_{t_0}^{t} n_{H_2,\text{reaction}}(t) dt}{9 \cdot n_{H_0-\text{DBT}}}$$
 (2)

In Equation (2), $n_{\rm H_2,reaction}(t)$ represents the amount of hydrogen consumed at time t as measured by mass-flow-meter. $n_{\rm H0-DBT}$ was calculated from $m_{\rm H0-DBT}$ the mass of H0-DBT provided in the reactor.

In the here reported batch mode experiments, hydrogenation is characterized by a constant reaction rate at the beginning of the reaction, that is, for low to medium degrees of hydrogenation. The gradient of DoH versus time is almost constant until a DoH of 0.6. This observation is further confirmed by the constant hydrogen consumption, as shown in Figure 6. This zero-order-like behavior hints for the fact that transport of hydrogen gas into the liquid phase limits the observed macrokinetics during the period of maximum hydrogen consumption at the beginning of the reaction. Further hydrogenation beyond the DoH of 0.6 is significantly slower owing to the falling concentration of hydrogenable LOHC left, but full conversion is always reached. The time to full conversion is a function of hydrogen pressure, reaction temperature, stirrer speed, and the molar catalyst to LOHC ratio.

The effect of hydrogen pressure on the rate of H0-DBT hydrogenation is shown in Figure 6 for experiments conducted at 180 °C and a molar catalyst to LOHC ratio of 1:400, corresponding to 0.25 mol% of the applied, commercial Ru/Al₂O₃ (5 wt%ruthenium) catalyst. It is apparent that a higher hydrogen pressure leads to faster hydrogenation and complete formation of H18-DBT is achieved in a shorter time. Full conversion is reached after 100 min (50 bar \approx 5 MPa), 140 min (40 bar \approx 4 MPa) or about 3 h at 30 bar hydrogen pressure. A reduction of hydrogen pressure below 30 bar leads to a massive increase in reaction time for full DOH under otherwise identical reaction conditions.

As can be seen in Figure 7, a linear relation between pressure and reaction rate is found for hydrogen pressures varying from 5 to 50 bar (0.5–5 MPa). Further investigations of hydrogenation reactions applying hydrogen pressures of less than 5 bar \approx 0.5 MPa not only show poor reaction rates but also seem to be affected by equilibrium limitations.



Figure 6. Hydrogenation of H0-DBT at different hydrogen pressures; $T = 180 \degree$ C, 5.9 mol DBT, 0.25 mol% Ru applied as 5 wt% Ru on Al₂O₃.

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Figure 7. Effect of hydrogen pressure on hydrogenation of H0-DBT; T = 180 °C, 5.9 mol DBT, 0.25 mol % Ru applied as 5 wt % Ru on Al₂O₃, 3 h reaction time.

To evaluate whether H0-DBT hydrogenation is a suitable method to purify hydrogen from hydrogen/methane mixtures out of the CMD process, our next set of experiments was dedicated to batch reactor hydrogenation studies using hydrogen/ methane mixtures. As shown in Figure 8, no negative impact of methane on the reaction rate or H0-DBT conversion was observed for comparative experiments in which 20 bar \approx 2 MPa of methane were added to 40 bar \approx 2 MPa of hydrogen. During these runs ($p_{H_2} =$ 40 bar, $p_{CH_4} =$ 20 bar) even a remarkable increase of the reaction rate was observed at low degrees of H0-DBT conversion.

Figure 8 clearly illustrates increased reaction rates for both experiments applying a mixed gas phase hydrogen substrate. Compared to the runs with pure hydrogen, higher degrees of hydrogenation were achieved after given reaction times. Further experiments featuring different methane partial pressures (see the Supporting Information) did not reveal any further influence on reaction rate or reaction time (until full hydrogenation was reached). In addition, the influence of stirrer speed was examined using the same hydrogen/methane mixture (40 bar hydrogen/20 bar methane). Increase in stirrer speed



Figure 8. Comparison of hydrogenation performance by using pure hydrogen and a hydrogen/methane mixture; T = 180 °C, 5.9 mol DBT, 0.25 mol % Ru applied as 5 wt % Ru on Al₂O₃.

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from 700 rpm (standard reaction conditions) to 900 or 1100 rpm, led to a linear increase of hydrogen consumption at the beginning of the hydrogenation (see the Supporting Information for details). This confirms the hypothesis that hydrogen gas mass transport into the liquid phase limits the observed reaction rate under the applied conditions. Moreover, it indicates that the increased rate in presence of methane gas is related to a faster mass transfer of hydrogen into the liquid phase very probably owing to a lower viscosity of the methane-saturated LOHC mixture compared to the methane-free system.

Conclusions

Our contribution highlights the fact that a combination of catalytic methane decomposition (CMD) and hydrogen purification and storage by hydrogenation of LOHC systems offers a versatile, economically attractive, and new way for upgrading stranded gas towards green, CO_2 -free hydrogen production.

Whereas the CMD step has been shown to operate in steady-state for at least 5 h converting 14% of the offered methane into hydrogen and carbon, the LOHC charging step operates beneficially with diluted hydrogen/methane streams to hydrogenate dibenzyltoluene to perhydro-dibenzyltoluene.

In the scenario of a stranded gas resource, for example, at an off-shore oil platform or at a remote drilling site in the desert, methane would be converted in the proposed technology sequence into carbon rich metal (for metallurgic processes) and transportable hydrogen in the form of a hydrogen-rich organic liquid.

It is fair to note, though, that nearly all studies on CMD to date have been performed at ambient pressure as an increase in total pressure is expected to have a detrimental effect on the reaction rate owing to thermodynamic effects.^[38] Actually, CMD conducted under pressure is a largely uninvestigated field of research in the area of methane decomposition. Therefore, it is expected that some compression of the methane/hydrogen mixture from CMD is required to provide the pressure for the hydrogenation step. However, the energy input into this compression step will depend on the compression ratio and with that the starting pressure delivered by the CMD step is important. This turns studies of CMD under even slight pressures into a highly relevant field for further investigations.

Experimental Section

Catalytic methane decomposition

The 20 wt % Ni/Al₂O₃ catalyst used in this work was prepared by incipient wetness impregnation of γ -Al₂O₃ (Sasol Germany) with an aqueous solution of Ni(NO₃)₂·6H₂O (Sigma–Aldrich). Prior to impregnation the γ -Al₂O₃ spheres were ground and sieved to a particle size of 500–630 µm. The impregnated sample was dried at 100 °C for 24 h and subsequently calcined at 500 °C for 4 h. The metal loading was verified by inductively coupled plasma atomic emission spectroscopy (ICP-AES). Prior to reaction the catalyst was reduced in a 50 mLmin⁻¹ hydrogen (Air products) stream for 2 h.



The methane decomposition experiments were carried out at atmospheric pressure in a fixed-bed quartz reactor (internal diameter: 11 mm, length: 700 mm) at temperatures ranging from 550 to 700 °C. 0.44 g of catalyst, corresponding to a bed height of 5 mm was used for each run. The feed consisted of pure methane (grade 3.5 corresponding to a purity of >99.95%, Westfalen AG) adjusted to a gas hourly space velocity (GHSV) of 12500 h⁻¹. The composition of the outlet stream was analyzed by an on-line gas chromatograph (Bruker 456-GC) equipped with two thermal conductivity detectors. No methane decomposition products other than hydrogen were detected in the effluent gas during the experiments. TEM studies were performed using a JEOL JEM-2200FS high resolution, aberration corrected transmission electron microscope.

LOHC hydrogenation

The hydrogenation experiments were performed by using a 5.3 L stainless-steel batch autoclave applied with a gas inducing stirrer (Büchi Glas). All experiments were performed with a 5 wt% Ru/ Al₂O₃ hydrogenation catalyst supplied by Alfa Aesar. The molar catalyst to LOHC ratio was constant at 1:400 (0.25 mol%). The pressure vessel was filled with catalyst and approximately 5.9 mol fully dehydrogenated DBT (Sasol Germany). Inert atmosphere was ensured by repeatedly purging the reactor with nitrogen (grade 5.0 corresponding to a purity of >99.999 %, Linde AG). The reactor was heated to reaction temperature using a thermostat (Julabo HT60 M2) and then pressurized with hydrogen (grade 5.0 corresponding to a purity of > 99.999 %, Linde AG) in a range of 1 to 55 bar (0.1-5.5 MPa). In case of the hydrogenation experiments applying a hydrogen/methane mixture, the pressure vessel was pressurized with a defined amount of methane (grade 2.5 corresponding to a purity of > 99.5 %, Linde AG) resulting in a pressure in the range of 5 to 55 bar (0.5-5.5 MPa). Subsequently hydrogen was induced to achieve a total pressure of 60 bar (6 MPa). During the experiment, pressure was kept constant by continuous dosing of hydrogen while measuring the hydrogen flow by use of a Bronkhorst® Mass Flow Meter (F-111AC).

Samples of the liquid phase were withdrawn periodically during the reaction and analyzed by using a JNM-ECX 400 NMR spectrometer (Jeol Ltd.).

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CONCEPTS



LOHC it in: Combining catalytic methane decomposition with hydrogen purification and storage by hydrogenation of LOHC systems offers a versatile and economically attractive way for upgrading stranded gas towards green, $\rm CO_2^-$ free hydrogen production.

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Carbon Dioxide-Free Hydrogen Production with Integrated Hydrogen Separation and Storage

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