Catalytically upgraded landfill gas as a cost-effective alternative for fuel cells

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ABSTRACT

The potential use of landfill gas as feeding fuel for the so-called molten carbonate fuel cells (MCFC) imposes the need for new upgrading technologies in order to meet the much tougher feed gas specifications of this type of fuel cells in comparison to gas engines. Nevertheless, MCFC has slightly lower purity demands than low temperature fuel cells. This paper outlines the idea of a new catalytic purification process for landfill gas conditioning, which may be supposed to be more competitive than state-of-the-art technologies and summarises some lab-scale results. This catalytic process transforms harmful landfill gas minor compounds into products that can be easily removed from the gas stream by a subsequent adsorption step. The optimal process temperature was found to be in the range 250–400 °C. After a catalyst screening, two materials were identified, which have the ability to remove all harmful minor compounds from landfill gas. The first material was a commercial alumina that showed a high activity towards the removal of organic silicon compounds. The alumina protects both a subsequent catalyst for the removal of other organic minor compounds and the fuel cell. Due to gradual deactivation caused by silica deposition, the activated alumina needs to be periodically replaced. The second material was a commercial V_2O_5/TiO_2-based catalyst that exhibited a high activity for the total oxidation of a broad spectrum of other harmful organic minor compounds into a simpler compound class "acid gases (HCl, HF and SO_2)", which can be easily removed by absorption with, e.g. alkalised alumina. The encouraging results obtained allow the scale-up of this LFG conditioning process to test it under real LFG conditions.

1. Introduction

The main driving force for the utilisation of landfill gas (LFG) is to avoid greenhouse gas emissions and to lower gas emissions with extremely high ozone depletion potential (ODP). Due to the fact that most landfills are found outside urban areas, the utilisation of heat from gas engines is barely possible. That is why fuel cells (FC) with a better power to heat ratio in comparison to gas engines seem to be very attractive in a prospective view. Additionally, in the recent years there has been an increasing need for a decentralised power supply and the search for alternative sources of energy in order to improve the current efficiencies (heat and power utilisation)

[1] and to mitigate the dependency to non-renewable fuels (e.g. oil and coal), respectively. This has driven companies and governments to look at renewable sources, such as biogases as an attractive energy source. Among the various types of biogases, landfill gas (LFG) appears as a promising but equally challenging alternative for fuel cells [2]. Its utilisation may not only reduce uncontrolled emissions of greenhouse gases and help to mitigate the dependency to fossil fuels but also to eliminate the wide range of pollutants found in this type of gas, which pose a threat to human health. According to the German Ministry of Environment (BMU), in the year 2007 around 1.143 million tonnes of CO_2 were saved in Germany due to the utilisation of landfill gas [3].

The main constituents of LFG are methane (40–60%) and carbon dioxide (35–50%) [4]. Additionally, LFG contains small amounts of oxygen (0–3%), nitrogen and is saturated with water vapour. The high energy content makes it an interesting energy source [5]. Due to its characteristics, LFG is already widely utilised in gas engines and turbines to produce electricity and heat [6].

The application of LFG into molten carbonate fuel cells (MCFC) would enhance the overall energy conversion efficiency. Compared to other fuel cell types, the MCFC is the most adequate fuel cell technology for LFG utilisation due to its high operation temperatures (600–700 °C) and higher flexibility regarding feeding fuels and it also has lower purity demands. MCFCs are uniquely suited
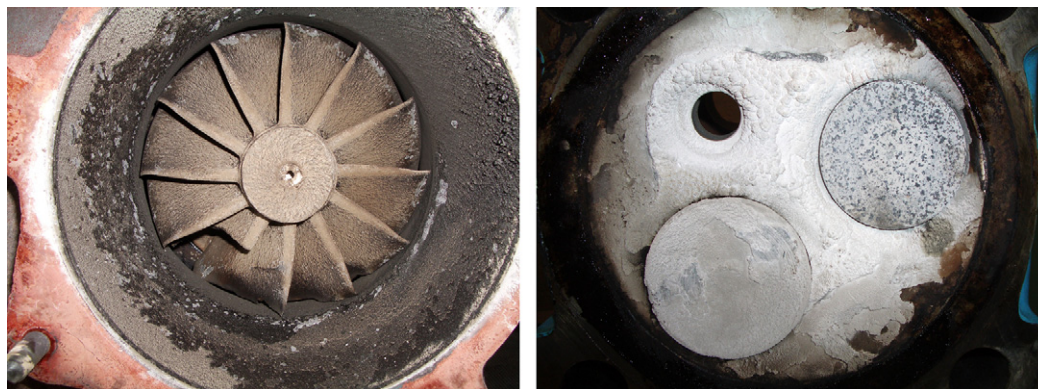
Fig. 1. Damaged blade wheel of a turbine caused by acid corrosion (left), SiO_2 deposition on a cylinder head caused by siloxane decomposition (right), both after more than 3500 h of operation.

for biogas applications, because no significant derating of power output is expected due to the methane dilution by CO_2 in LFG. In addition, the presence of CO_2 at the cathode raises the electrical efficiency [7]. MCFC technology is near to commercialisation, and the elevated temperatures make the use of noble metal catalysts unnecessary [8].

Apart from the main components, LFG also contains relatively high amounts of hydrogen sulphide and a broad spectrum of volatile organic compounds (VOC): organic-sulphur compounds (e.g. carbonyl sulphide, mercaptans), silicon-containing compounds (e.g. siloxanes), halogenated compounds, aromatics and aliphatic hydrocarbons [4,9]. The utilisation of biogases like LFG for power generation may result in damages for the downstream power generating units, since during combustion the halogenated compounds and sulphur-containing compounds are transform into acid gases like H_2SO_4, HCl and HF, which cause corrosion problems. In addition, siloxanes are transformed into micro-crystalline silica, which deposits on the engine parts contributing to abrasion and poorer combustion efficiency. Fig. 1 shows typical damages caused by acid corrosion and the deposition of siloxane decomposition products (microcrystalline SiO_2) on turbine and gas engine parts after 3500 h of operation. This type of damages results in shorter lifetimes for the machinery, more frequent maintenance and subsequently, in higher operating costs. Due to the lower tolerance to impurities, the utilisation of LFG in conjunction with MCFCs with the present state-of-the-art gas qualities would result in poisoning of the reformer catalyst in only a few hours of operation.

For this reason, the harmful trace contaminants have to be removed by a suitable purification process, before landfill gas can be used in MCFCs. These trace compounds have been shown to be very harmful for MCFCs [10,11]. Present upgrading processes for landfill gas such as cooling, adsorption or absorption with inorganic and organic solvents are designed for the conditioning of LFG to a combustion engine gas quality. Furthermore, these state-of-the-art technologies often fail because of technical or economic reasons, for example, low removal efficiencies, or high operational costs [12]. They appear to be unsuitable to fulfil both the technical and economic demands of landfill gas utilisation in MCFCs.

Catalytic removal of minor compounds from LFG appears as a cost-effective and attractive alternative solution for the cleanup of LFG, since such catalytic process would reduce the complex LFG matrix of minor compounds into one compound class (acidic gases), which can be easily removed by state-of-the-art technologies like adsorption or absorption.

Even though noble metals and metal oxides are widely used to eliminate VOCs by catalytic oxidation [13,14], to our knowledge only a few studies regarding catalytic LFG clean-up have been published. The applicability of several commercial oxidation catalysts has been evaluated in a field-test plant to oxidise LFG minor compounds to reactions products such as HCl, HF, and SO_2 [15] showed encouraging results. The acidic reaction products were removed by using a water scrubber device.

In general, V_2O_5/TiO_2 and V_2O_5–WO_3/TiO_2 catalysts are active for the combustion of VOCs [16] and the most largely used catalytic systems for the oxidation of chlorinated VOCs [17]. Therefore, two V_2O_5/TiO_2-based catalysts were chosen among a large variety of commercial oxidation catalysts for testing at the lab scale.

An alternative way to upgrade LFG to fuel cell quality is the combination of catalytic hydro-processing and the use of disposable adsorbents for the removal of the acidic reactions products H_2S and HCl [18]. However, this process needs additionally hydrogen as reactant, whereas a catalytic oxidation/hydrolysis process can use for the degradation of VOCs, oxygen and water vapour which are normally contained in LFG. The main problems of using catalytic processes for LFG purification are the irreversible and rapid deactivation of the catalysts by deposition of siloxane degradation products on the catalyst surface (microcrystalline silica). Thus, a previous abatement process for siloxane removal is necessary.

For this reason Fraunhofer UMSICHT is developing a combined process that consists of three steps: (1) siloxane abatement at around 300 °C, (2) catalytic oxidation/hydrolysis of the remaining trace compounds at 300 °C, and (3) removal of the acidic reaction products by adsorption/absorption on alkalised media.

2. State-of-the-art technologies

Current state-of-the-art gas treatments fail to upgrade landfill gas up to a fuel cell quality. There are many reasons for it, but the economical factors are perhaps the most decisive, since up to date no purification system is able to eliminate all the minor components present in LFG, it resulting in the implementation of sequential steps, which target specific substances, for example dehumidification, desulphurisation, siloxane removal and VOCs removal. Moreover, a purification system must be able to cope with concentration peaks, which are usually observed in landfill gas for this kind of pollutants.

2.1. Adsorption methods

Among all the conventional purification processes, the application of active carbon alone or in combination with chilling systems is perhaps the most common methodology for the removal of pollutants from landfill gas. Although commercial active carbons are fairly cheap, one of the drawbacks of its application is the relatively low capacity towards the most damaging substances, such as siloxanes, halogenated compounds and sulphur-containing compounds,

although impregnated active carbons are known to have high selectivity towards H_2S [19]. It is due to the competing adsorption effects that take place in the carbon matrix, since the aliphatic hydrocarbons and the aromatics present in landfill gas, which are found in relatively high concentrations, are favourably adsorbed, thus resulting in shorter breakthrough times for the more harmful substances and therefore higher operational costs. For conventional active carbons, the presence of water reduces significantly the adsorption capacities towards aromatics [20].

It is worth mentioning that active carbon is not a definite solution from an environmental point of view because the pollutants adsorbed have to be disposed after saturation of the material. The most common way of treating used active carbon is by burning it, which means that the pollutants are oxidised producing new dangerous substances, and thus, not really solving the problem, since it is shifted to the waste incineration plants.

Other materials like silica gel have shown comparable siloxane removal capacities ($100\,mg\,g^{-1}$) to active carbons with the advantage of being regenerable by thermal treatment [21]. However, due to their hydrophilicity, the adsorption capacities are remarkably reduced.

2.2. Absorption methods

Water scrubbing processes are reasonably applicable to gases containing high concentrations of H_2S, recovering sulphur through oxidation. For less concentrated gases this technology seems to be less convenient. Water has a relatively good efficiency for H_2S removal, but CO_2 is also absorbed and hence, for the case of LFG it is unsuitable. Moreover, large water volumes are needed and reboiling is necessary for regeneration. For other LFG impurities very poor removal efficiencies are achieved because of their low solubilities in water and high vapour pressures. Absorption methods have been applied for the removal of target substances like siloxanes, where concentrated solutions of acids and bases have shown to have moderate removal efficiencies or the application of organic solvents at high temperatures. Nevertheless, in all cases their utilisation complicates plant design due to safety concerns and hence incurring in higher operational costs. Moreover, for the case of alkaline solutions, the presence of carbon dioxide in landfill gas makes its implementation unpractical. The application of gas scrubbing with organic solvents have shown to be disadvantageous since the more volatile siloxanes, such as hexamethyldisiloxane (L2) or trimethylsilan may be stripped into the gas phase at high gas flow rates [12].

2.3. Chilling processes

The application of cooling systems is usually carried out in order to remove water and thus avoiding corrosion damages in engine parts. Parallel to water removal other substances, such as heavy aromatics and siloxanes can be at least partially removed. It has been shown [12] that at $-25\,°C$ a removal of 25.9% for volatile methyl siloxanes (VMS) is possible and that a removal of around 99% can only be achieved by freezing temperatures as low as $-70\,°C$. According to Schweigkofler [22] 89% of the silicon compounds in a dried gas can be removed by a cooling temperature of just $5\,°C$. Higher removal efficiencies are achieved at lower temperatures. Previous studies carried by Siloxa Engineering AG and Fraunhofer Institute UMSICHT [23] have shown that freeze-cooling systems for the removal of siloxanes are only cost-effective in combination with active carbon in the scenario of high flow rates with relatively high loads of siloxanes. In general, the energetic requirements for the application of deep chilling systems are so high that such process, as experience for the case of sewage gas [24] is not profitable.

2.4. Catalytic process

Although VOCs are usually destroyed by catalytic methods, a complex matrix such as landfill gas makes their removal more challenging, since many minor components present in LFG act as poisons even for non-noble metal oxides. That may explain why catalytic systems are relatively unusual at landfill sites. Fraunhofer UMSICHT has been designing a catalytic system, which may remove all minor components present in landfill gas without compromising the methane contained in it. Due to the process characteristics and the final gas quality and composition it is thought that a coupling with a molten carbonate fuel cell would enhance the overall energetic utilisation.

The process consists of three main stages:

1. Siloxane removal: a cheap catalyst material dedicated to the catalytic decomposition of siloxanes has been identified, which has shown very good performance and higher capacities than conventional active carbons at working temperatures around $300\,°C$. Additionally, this material exhibits catalytic activity towards the removal of other minor components such as H_2S, C_2Cl_4, terpenes and aromatics. Due to the SiO_2 deposition, the material has to be periodically exchanged. Therefore, regeneration of the activated alumina is not possible since the SiO_2 microcrystals deposit on the microporosity damaging irreversibly the active sites of the material. However, the very low price of this material makes regeneration unnecessary.
2. In the second stage, the siloxane-free gas, which still contains VOCs and sulphur-containing compounds is oxidised at around $300\,°C$ to form HCl, HF and SO_2 over a vanadium-based catalyst without compromising the methane content. Regeneration of the vanadium-based catalyst is in principle possible as long as oxygen is present in the system in excess in order to oxidise the VOCs. Thus, in situ regeneration may take place enhancing the lifetime of the catalyst. However, a regeneration step at the second stage has been considered as a future prospect.
3. As last stage, an alkalised material can be used to selectively remove the acid gases produced during the oxidation process. As a result, the previously complex LFG matrix has been reduced to the simpler gas mixture CH_4/CO_2. A simplified sketch of the catalytic process is depicted in Fig. 2. The acid gas removal is a state-of-the-art technology and therefore, not investigated in detail since all the market available products exhibit very good absorbing capacities.

The reaction temperature was so chosen since a shift in behaviour in a higher range of temperatures is expected since the catalyst stability may be affected by thermal effects like sintering. Moreover, deactivation by high temperature reactions may occur. Additionally, the methane – which is the fuel – may be oxidised and depleted considerably at higher temperatures. Furthermore, due to the oxygen excess (in relation to the minor compounds), a change in temperature plays a relatively small role for the oxidation of minor compounds.

By changing the space velocity only conversion of the minor compounds was lower but no by-products were observed. Besides, it has been observed that as long as oxygen is present in excess no by-products are formed and therefore, other temperatures are of no interest due to methane oxidation. Large space velocities are no profitable and low space velocities result in long residence times.

In addition, this catalytic purification process was developed because the waste heat produced by the fuel cell ($\sim480\,°C$) can be used to pre-condition the raw landfill gas ($20\,°C$), thus enhancing the overall efficiency of the process. A description of the gain in effi-

purified landfill gas

3

Cl⁻, F⁻, SO₃⁻/SO₄⁻

Separation of acid gases
HCl, HF, SO₂

2

300°C

VOC oxidation
H₂S removal

1

SiO₂

siloxane removal

landfill gas contains more than
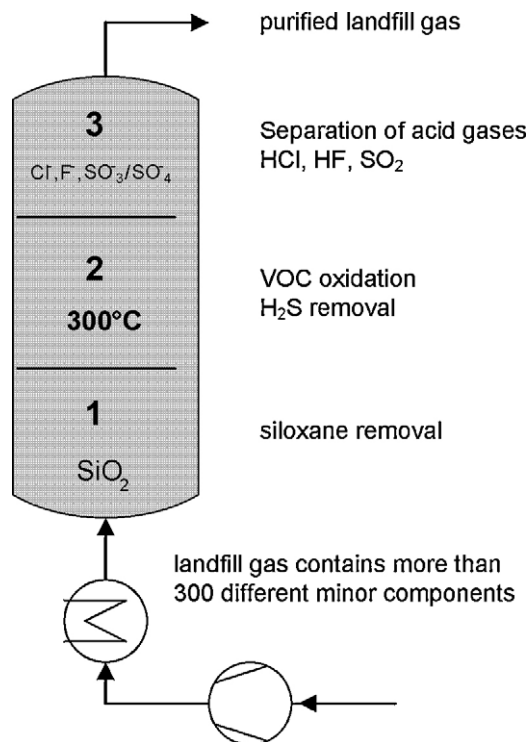300 different minor components

Fig. 2. Simplified sketch of the three-step catalytic process for LFG conditioning.

ciency through waste heat utilisation has been shown elsewhere [25,26].

3. Experimental

3.1. Materials and methods

The lab-experiments were carried out in a custom-made setup (see Fig. 3). With this setup it was possible to monitor online the oxidation of the model compounds of a simulated landfill gas. The model substances used for the tests to represent the typical minor compounds were hydrogen sulphide (H_2S), benzene, toluene, tetra-chloroethylene (TCE) and the chlorofluorocarbon CFC-113, which were enriched into the system by conventional evaporation with a similar setup as that one used by Schweigkofler [22]. Among different factors, one of the reasons why the selected substances were chosen as representative of the LFG minor compounds, was to choose those minor compounds that are either chemically stable (more challenging to convert) or found in relatively high concentrations in LFG from every compound class. Availability of the chemicals was another important criterion since for the case of many chlorofluorocarbons their purchase is not longer possible due environmental regulations. The authors considered the chosen model compounds as good representatives of the different compound classes found in LFG, for example, benzene as stable aromatic compound, R113a as a stable and still available FCC, H_2S as the sulphur-containing compound present in higher concentration in LFG and L2 and D4 as typical siloxanes (linear and cyclic) found in LFG.

All model compounds were purchased from Sigma–Aldrich with reagent grade. Hydrogen sulphide (1000 ppm) supplied by Air Liquide was added directly from a gas cylinder into the feed gas flow. All the other gases were purchased from Linde Gas with the following technical qualities: N_2 (5.0), CH_4 (2.5), CO_2 (n.a.), O_2 (3.5). With this setup it was possible to generate dry or humid simulated LFG. The gas composition of the simulated LFG at the inlet and outlet was monitored with a chemical-ionisation mass spectrometer (CI-MS) model Airsense 500 from the company MS4-Analysentechnik, Rockenberg, Germany. Three ionisation gases (Xe, Kr and Hg) were used as ionisation agents depending on the ionisation energies of the different compounds. The advantage of the CI-MS is that one measures directly the molecular mass and no fragments as with conventional electron ionisation MS. This allows a simultaneous online measurement of reactants and products.

Controlling software (HP data acquisition in lab, Siemens SPS S7 in the field test) was used to generate the desired gas mixtures by controlling the mass flow controllers (Type MFC-D-5111 from M&W Instruments) and to set the temperatures at the reactor, pipe lines and humidifier. In the field-test facility, the real LFG was obtained from the landfill site provider through a pipeline installed before the dehumidification system. The LFG was then compressed and guided to the reactors in the container. The test facility could be operated in series or parallel. To monitor the changes in concentration before and after every reactor a multi-position valve (MPV) was used to select the desired gas for the analysis. In order to accelerate the breakthrough of the selected siloxanes a similar evaporation system as that one used in the laboratory was utilised for the enrichment of the LFG before reactor 1. The gas flow rate at the inlet of reactor 1 was around 18.5 Nl min⁻¹ and the inlet concentrations of the enriched siloxanes L2 and D4 were ca. 230 ppmv and ca. 110 ppmv, respectively. To determine the trace compound concentrations at the reactor inlet and outlet the CI-MS was used alone or in combination with two gas chromatographers, one equipped with a thermal conductivity detector (Micro-GC-TCD, "Quad Series" from Agilent) for the measurement of the LFG main components and an Agilent 6890 GC-FID/ECD (with a flame ionisation detector and a electron capture detector) for the analysis of the trace compounds.

The surface area of the different catalysts tested was characterised by nitrogen adsorption at 77 K following the BET model after degassing for 4 h at 200 °C in order to eliminate water and any other substance adsorbed at the surface. Energy dispersion X-ray characterisation was used to determine the capacities of the exhausted materials.

4. Results and discussion

4.1. Lab-scale experiments

4.1.1. Catalytic oxidation of VOCs

Two commercial V_2O_5–TiO_2 catalyst were tested in a lab-scale tubular reactor (see Fig. 3) of dimensions: length = 500 mm and
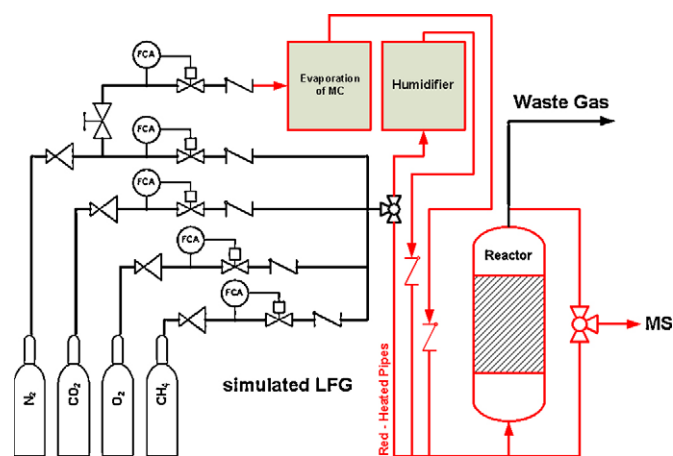
Fig. 3. Sketch of a custom-made setup used for monitoring the catalytic oxidation of model LFG minor components.

Table 1
Characteristics of the catalysts chosen for VOC oxidation.

	V_2O_5 [wt.%]	TiO_2 [wt.%]	Diameter [mm]	BET surface [$m^2\,g^{-1}$]
Catalyst A	12.0	75.0	4.0	200
Catalyst B	20.5	Balance	1.6	47

internal diameter = 17 mm. Table 1 summarises important properties of the catalysts. Catalyst B is composed by V_2O_5 and TiO_2 only, whereas catalyst A contained also significant amounts of WO_3, MnO_2, CuO, and Fe_2O_3. These metal oxides may act as promoters to enhance the activity of the catalyst.

The simulated LFG (45% methane, 25% carbon dioxide, 1% oxygen, balance nitrogen) was obtained by mixing different volume flow rates of methane, carbon dioxide, nitrogen and oxygen via mass flow controllers. Experiments were carried out with and without water vapour. The reaction temperature was always 300 °C to ensure both a sufficient activity of the catalysts and avoid any degradation of methane. In Table 2 are listed the results for the oxidation of minor compounds with catalyst A.

Catalyst B was tested with a simulated landfill gas. It showed comparable conversion rates for most of the used model substances in presence of oxygen (see Table 3), except for CFC-113. It was expected that testing the activity of the catalyst B in presence of water would show similar results compared to catalyst A. For this reason, the tests with catalyst B were not continued.

Depending on the reactant (oxygen or water) in the feed gas, catalyst A showed clearly for benzene and CFC-113 different conversion rates. It is apparent that water vapour is necessary as reactant to obtain the maximum activity of catalyst A for the degradation of CFC-113. In contrast, benzene was only catalytically converted when an excess of oxygen was present in the water-free feed gas. It is well known that the presence of water in the feed gas leads to a change of the active centres at the surface of a metal oxide catalyst. The dissociative adsorption of water on the coordinatively unsaturated cations and anions at the catalyst surface leads to the formation of Brønsted acid centres and causes the disappearance of Lewis acid centres [27].

For the decomposition of CFC-12 on a TiO_2 catalyst in presence of water a suggested mechanism starts with the adsorption of CFC-12 on a Brønsted acid centre followed by a reaction of the adsorbed CFC-12 with neighbouring surface hydroxyls to produce intermediates such as $COCl_2$, which further react to form complete oxidation products [28]. The results in the present study seem to confirm in a qualitative manner that CFC-113 will be decomposed via a similar mechanism. A detailed investigation of the reaction mechanism was not the aim of this study.

For the oxidation of aromatic compounds such as benzene, it is essential the presence of coordinatively unsaturated cations and anions at the catalyst surface. To break an aromatic nucleus a V^{5+} cation should be surrounded by several oxygens which make an abstraction of hydrogens with a rupture of an aromatic ring possible [29]. It is to be expected that hydroxylation of coordinatively unsaturated cations and anions by water suppress the oxidation of aromatic compounds as indicated by the conversion rates for benzene in Table 3.

To verify the different effects of water vapour and oxygen on the conversion of LFG minor compounds, further experiments have to be conducted in a field-test facility. Interestingly, the conversion rate of TCE seems to be almost independent of the experimental conditions. This could indicate that there is no competitive adsorption between water and TCE for the active centres or TCE can use active centres both before and after hydroxylation by water.

The selectivity of the catalysts for the formation of complete oxidation products could only be determined in a qualitative way. SO_2 and H_2O were the only reaction products that were detected during the oxidation of H_2S. Benzene was oxidised to CO_2, CO and H_2O. The oxidation/hydrolysis of the halogenated model compounds TCE and CFC-113 leads to the formation of the desired reaction products CO_2, HCl, HF. However, partially oxidised reactions products such as $COCl_2$, COF_2 and Cl_2 were detected when the gas mixtures were at under-stoichiometric conditions. These products are both toxic and hard to remove by a subsequent adsorption process. For this reason, one of the most important tasks in prospective catalyst tests is the quantitative determination of the product distribution after oxidation/hydrolysis of the LFG minor compounds. For further experiments in a field-test plant, catalyst A has been chosen, because it showed even for a stable compound like CFC-113 significant conversion rates. The results obtained are very encouraging but it is clear that improvements have to be made in order to achieve fuel cell gas quality. Therefore, parallel experiments were carried out in a field-test facility with real LFG in order to test the performance of the selected catalyst towards VOC oxidation and a new chosen material for the removal of siloxanes.

4.1.2. Siloxane removal

During the lab-scale tests, a field-test facility was built in order to test catalysts with real LFG towards siloxane removal. The main components of the test facility are two tubular reactors (length = 760 mm, internal diameter = 60.3 mm). The reactor inlets and outlets are connected via a multi-position valve (MPV) to a mass spectrometer so that the gas composition at these four points

Table 2
Catalytic activity of catalyst A towards removal of model minor compounds.

Model compound	Concentration [ppmv]	Carrier gas N_2 [$ml\,min^{-1}$]	O_2 [$ml\,min^{-1}$]	H_2O_v [$ml\,min^{-1}$]	MC:reactant	Conversion [%]
TCE	213	504	10		1:91	97
TCE	208	504		0.8	1:73	88
CFC-113	183	504	10		1:106	78
CFC-113	185	504		0.8	1:8	40
Benzene	202	504	10		1:76	99.8
Benzene	200	504		0.8	1:6	~0
H_2S (with 100 ppmv O_2)	45	504			1:2	~100

Table 3
Catalytic activity of catalyst B towards removal of model minor compounds.

Model compound	Concentration [ppmv]	LFG total [$ml\,min^{-1}$]	O_2 fraction [$ml\,min^{-1}$]	Conversion [%]
TCE	219	1000	10	93.2
CFC-113	189	1000	10	1.4
Toluene	351	1000	10	99.8
H_2S	107	1000	10	~100

Fig. 4. Simplified diagram of the field-test facility.

Fig. 5. Conversion rates of the siloxanes L2 and D4 on activated alumina.

can be individually measured. LFG is fed in the test facility by a compressor. A simplified diagram of the field-test plant is shown in Fig. 4.

The LFG used in the field-test experiments was characterised in order to know the composition and time variation of the major and minor compounds. Table 4 summarises the characterisation results. From Table 4 it can be seen that the major compounds exhibit similar values as those reported in literature. For the case of minor compounds, the LFG shows relatively high loadings of H_2S, aromatics and terpenes. The two analyses were carried out with a time difference of nearly a month.

A test series was conducted in order to find a suitable and relatively cheap material, which abates siloxanes. A screening of different materials included one alkalised bentonite, two bleaching earths, corundum, two titanium dioxide catalysts, an aluminium silicate and an activated alumina. In each case, 250 g of the materials were filled up into the first reactor that was operated individually. The materials were tested with LFG that was additionally enriched

Table 4
Determination of the concentrations of major and minor components in a dry LFG and their time variation.

Major components	Analysis I [vol.%]	Analysis II [vol.%]
Methane	54 ± 1	53.3
Carbon dioxide	35 ± 1	32.9
Oxygen	0.89 ± 0.05	0.7
Nitrogen	11.0 ± 0.5	13.0
Minor components	Analysis I [mg m^{-3}]	Analysis II [mg m^{-3}]
Hydrogen sulphide	230.0	280.0
Isopropylbenzene	5.6	3.3
Limonene	25.0	15.8
Pinene	83.7	85.3
Benzene	3.4	4.7
Toluene	21.0	18.4
Xylene	45.0	35.6
Trimethylbenzene	13.4	8.0
Tetrachlorethene	0.14	0.3
Methanethiole	0.56	
Chlorobenzene	0.22	
Trichloroethene	0.24	0.5
D3	0.84	0.5
D4	15.0	10.6
D5	3.0	3.3
L2	5.0	3.1
L4	<0.005	<0.1
Trimethylsilanol	12	11.0

with the siloxanes D4 (octamethylcyclotetrasiloxane) and L2 (Hexamethyldisiloxane) as model compounds to shorten the test times. A carrier gas ($5 l h^{-1}$ nitrogen) flowed parallel through two tempered gas washing bottles that contained L2 and D4 (referred to as saturator unit in Fig. 4). The enriched nitrogen gas flow was mixed with LFG ($1.11 m^3 h^{-1}$). The resulting initial concentrations in the feed gas were 100 ppm D4 and 200 ppm L2. The reactor temperature was 300 °C.

Among all materials tested it was observed that the activated alumina exhibited the highest activity towards siloxane removal. Fig. 5 shows the conversion rates of the degradation of the model siloxanes L2 and D4. The initial conversion rate was 100% for both siloxanes, which gradually decreased due to the proceeding deactivation of the activated alumina. After 35 h the conversion rate for D4 dropped to approximately 9% and for L2 around 20%.

The activated alumina had the best performance for the conversion of L2, but the decrease in reactivity was not so fast in comparison with the decline of conversion activity for D4. It might be assigned to the fact that D4 produces per molecule twice as much SiO_2 as L2, thus the number of active centres at the surface of the activated alumina that are deactivated are theoretically two times higher. The initial conversion rates of L2 with the other materials were lower than the L2 conversion rate of the activated alumina and decreased in the first hours very quickly. Thereafter, the conversion rates stabilised, so that after 40 h conversion rates between 15% (bleaching earth I) and 35% (bleaching earth II) were measured.

In the framework on this material screening, a detailed description of the possible conversion mechanisms of the siloxanes L2 and D4 or the identification of the active centres was of no interest. The fundamental aim of this work is to find a cheap and high-performance material for the removal of siloxanes with a sufficient lifetime.

The silicon content of fresh and used activated alumina samples was measured by energy dispersive X-ray analysis (EDX). The BET method was used to determine the specific surface area. The volumes of the micro- and mesopores were obtained by analysing the nitrogen desorption isotherm with the methods of Horvath Kawazoe (HK) and Barrett, Joyner and Hallender (BJH). The macro pores volume was quantified by Hg porosimetry. The results are listed in Tables 5 and 6.

The EDX results clearly show that due to the deposition of siloxanes degradation products the silicon concentration of the used sample increased. Besides the specific surface area, the micro- and mesopores volumes of the activated alumina were also drastically reduced, whereas the macropores volumes are nearly unaltered.

Table 5
EDX results for fresh and used activated alumina.

Activated alumina	C [wt.%]	O [wt.%]	Al [wt.%]	Si [wt.%]	S [wt.%]
Fresh sample	5.42	51.78	42.68	0.13	–
Used sample	4.56	46.34	39.08	9.61	0.22

Table 6
Pore volumes and specific surface area of fresh and used activated alumina.

Activated alumina	Micropores volume [mm^3 g^{-1}]	Mesopores volume [mm^3 g^{-1}]	Macropores volume [mm^3 g^{-1}]	Specific surface [m^2 g^{-1}]
Fresh sample	110.3	110.8	33.3	268
Used sample	4.56	46.34	39.08	9.61

This indicates that the macropores are responsible for the transportation of the siloxanes into the pore system. The degradation of siloxanes followed by the deposition of the reaction products takes place in the micro- and mesopores.

Besides the solid reaction products two volatile reaction compounds were detected at very low concentrations: D3 (hexamethylcyclotrisiloxane) and trimethylsilanol (TMS). The formation of volatile reaction products is undesired, because they also may deactivate the subsequent metal oxide catalyst. Further experiments are being carried out in order to confirm these findings. The activated alumina also exhibited moderate activity for other LFG impurities that were monitored during the test (see Fig. 6). For example, the initial conversion rate for H_2S is around 87% but decreases rapidly and after approximately 10 h, the conversion is nearly zero. Many factors may play a role for this finding, since oxygen shortages may reduce the ability of the activated alumina to regenerate the active centres, thus resulting in poisoning by the accumulation of sulphur at the surface or competing adsorption effects may also take place. Moreover, the parallel deposition of SiO_2 reduces the number of active centres available at surface. For pinene and limonene, which are usually found in LFG in relatively high concentrations ($\sim$20–100 mg Nm^{-3}), the conversions were in the range 60–70% and 45%, respectively. Their conversion seems to be independent of the surface area reduction caused by the SiO_2 deposition. Similarly, halogenated and aromatic compounds exhibit relatively constant conversions, it indicating that the active sites at surface responsible for their conversion are still available, although it is assumed that in the presence of water the Lewis-acid centres (Al^{3+}) are transformed into Brønsted bases due to the adsorptive dissociation of water.

5. Conclusions

For the development of a catalytic LFG upgrading process two materials were identified, which showed a high potential for the removal of all LFG minor compounds that are harmful to MCFCs. Depending on the experimental conditions a commercial V_2O_5–TiO_2 catalyst possessed good activity for the oxidation/hydrolysis of organic and inorganic model compounds. A commercial activated alumina was able to remove high concentrations of volatile siloxanes, which have a deleterious effect on both, the V_2O_5–TiO_2 catalyst and a downstream MCFC. In further experiments, the selectivity of the degradation reactions for desired products such as HCl, HF and SO_2 must be quantitatively determined. Also the effects of the reactants water and oxygen for the complete oxidation of the different LFG minor compounds must be studied in detail in order to optimise the process. Finally, long-time tests must be conducted with real LFG to measure the lifetime of the materials and determine removal capacities.

According to the results, the catalytic purification process introduced could become a cost-effect alternative for LFG upgrading in contrast to traditional methods, but in order to prove it, field-test are underway.

Fig. 6. Catalytic conversion of other LFG impurities measured during the siloxane decomposition tests with activated alumina.

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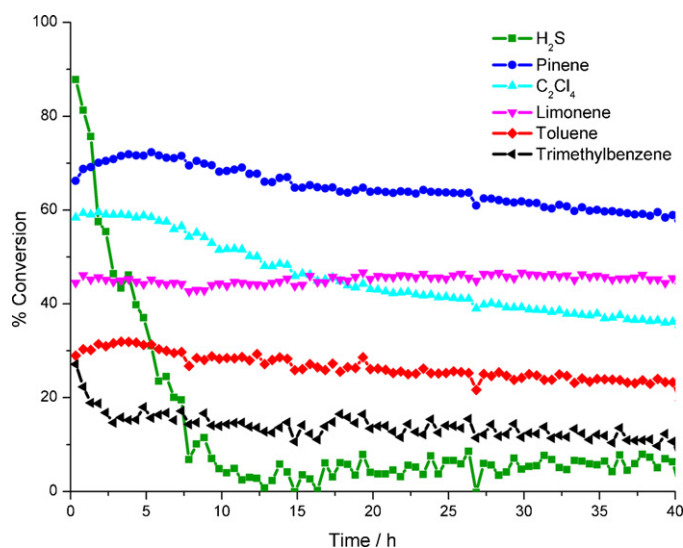[21] M. Schweigkofler, R. Niessner, J. Hazard. Mater. B83 (2001) 183–196.

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