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Catalytic hydrodechlorination of groundwater contaminants in water and in the gas phase using Pd/γ-Al_2O_3

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Abstract

Pd/γ-Al_2O_3 can be used as a hydrodechlorination catalyst for both the water and the gas phase. A comparison of the catalytic hydrodechlorination of 1,1,2,2-tetrachloroethane (TeCA) in water and in the gas phase at various temperatures with Pd/γ-Al_2O_3 revealed Arrhenius parameters identical for the reaction in both phases: $\ln(A_{\mathrm{Pd}}\ (\mathrm{l/(g\,min)})) = 22.8 \pm 0.9$, $E_A = 58.0 \pm 2.3\,\mathrm{kJ/mol}$. Catalysts are deactivated by sulphur compounds but can be fully regenerated by oxidative treatment at elevated temperatures. A selectivity shift depending on the catalyst deactivation state was observed: unsaturated chlorocompounds react with the highest rate on fresh catalyst, whereas on partially deactivated catalysts saturated compounds such as tetrachloroethane are most rapidly dechlorinated. Apparently, saturated and unsaturated chloroorganic compounds react via different mechanisms. The relative reactivities of the C–Cl and C–Br bonds in bromochloromethane (BCM) are temperature dependent. At a low temperature (100 °C) methyl chloride is the dominant side product, whereas at a higher temperature (200 °C) methyl bromide is preferred.

Keywords: Hydrodechlorination; Hydrodebromination; 1,1,2,2-Tetrachloroethane; Vinyl chloride; Bromochloromethane; Pd catalyst; Catalyst poisoning; Catalyst regeneration; Reaction selectivity

1. Introduction

Chlorinated organic compounds (COCs) are among the most widely distributed pollutants in wastewaters and contaminated groundwaters. Their effective removal and destruction is an important task. In the region north of Bitterfeld (Germany), an area of chlorine-based chemical industry for more than 100 years, there now exists a complex groundwater contamination pattern containing various COCs in extremely high concentrations. In addition to chloroethenes, components such as chlorobenzenes and chlorinated alkanes are the main groundwater contaminants, making in situ remediation using zero-valent iron barriers impractical. Catalytic hydrodechlorination using Pd catalysts may be an effective alternative for these compounds [1–6]. However, Pd catalysts applied directly in the groundwater suffer from relatively rapid deactivation [7–9], e.g. by sulphur poisoning and by interference from processes such as scaling and biofouling. Even embedding the Pd in hydrophobic poly(dimethylsiloxane) membranes or in hydrophobic zeolites did not provide sufficient protection for the noble metal [8,9].

A promising alternative is the transfer of COCs from the water phase into the gas phase, followed by catalytic hydrodechlorination using Pd-containing

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catalysts [10]. The catalyst can be identical for both the water phase and the gas phase. The gas-phase reaction has several advantages. At higher temperatures (100–350 °C), the reaction rate is significantly increased, with the consequence that the fixed-bed reactor can be very compact. Even those COCs which are practically inaccessible to reductive dechlorination in the water phase (e.g. CH_2Cl_2 and 1,2-$C_2H_4Cl_2$) react with adequate rates. Transport limitations in porous catalysts can be avoided due to the high diffusion rates in the gas phase. Finally, the reaction conditions preclude any direct interference from biological activities.

In the case of the particular groundwater under study, the main contaminant with a concentration of about 100 mg/l is 1,1,2,2-tetrachloroethane (TeCA), a compound which is not easily stripped (Henry's Law constant $K_H(20\,^\circ C) = 0.015$ [11]). The present work focuses on the catalytic hydrodechlorination of COC mixtures in water and in the gas phase over a broad temperature range (0–350 °C). Potential problems addressed include sulphur poisoning of the catalyst in the gas phase (from stripped S-compounds), competition between COCs and O_2 under hydrogen-deficient conditions, and product selectivity in dependence on the reaction temperature and catalyst state.

2. Methods

All reagents (methanol, toluene, COCs) were purchased in 99+ grade from Merck (Germany) and used as received. Pd on γ-Al_2O_3 (0.5 wt.% Pd, G-133 D) egg-shell catalyst in pellet form was purchased from Commercia (Suedchemie, Germany), pre-reduced with $NaBH_4$ in methanol, rinsed in deionized water and dried prior to use.

The studies in the water phase were carried out as batch experiments. Two hundred and fifty millilitres screw-cap bottles equipped with mininert® valves were used. One hundred and fifty to two hundred and eighty milligrams pulverized Pd/γ-Al_2O_3 catalyst (depending on the reaction temperature and the reaction rate) were added to 200 ml deionized water, which was saturated with H_2 by 30 min bubbling through the suspension. The headspace over the suspension was pure H_2. The mininert valve was closed and the bottle brought to the desired temperature. TeCA, chlorobenzene and toluene as internal standard were then added as methanolic solution, resulting in concentrations of 50 mg/l TeCA and 25 mg/l each of chlorobenzene and toluene. After adding the contaminants, the bottle was shaken well and placed back into the thermostat. The suspensions were vigorously stirred throughout the experiments to ensure negligible macroscopic transport resistance and sufficient H_2 supply from the headspace into the water phase. The water was frequently sampled by taking 500 μl solution, which was transferred into a PTFE-lined 2 ml vial. After shaking the vial in a thermostat at 25 °C for 2 min, 50 μl of the gas phase over the solution was analyzed by GC–MS (QP 5000, Shimadzu Corporation using a 30 m × 0.25 mm DB1 0.25 μm thin film capillary). The experimental and analytical procedures are based on two assumptions: (i) the proportion of COCs present in the headspace is small compared to that in the water phase (dimensionless Henry's law constant $K_H \ll 1$); and (ii) the H_2 demand for hydrodechlorination is small compared to the total hydrogen amount present in the reactor bottle (dissolved + headspace). Simple calculations show that these assumptions are valid.

The examination of the catalyst behaviour in the gas phase was carried out in the temperature range between 70 and 350 °C using a fixed-bed reactor made of stainless-steel tubing (6 mm × 1 mm) inside a tube furnace with a 10 cm isothermal zone (Fig. 1).

The reactor was filled with 500 mg Pd/γ-Al_2O_3 (original pellets crushed to 1–3 mm, dust removed). Pure H_2 or H_2/N_2 (1:5) mixtures were employed as carrier gas with a gas flow of 50 ml/min (gas flow controllers from Bronkhorst, The Netherlands), resulting in a hydrodynamic residence time of $\tau \leq 1$ s of the gas in the catalyst bed (space velocity ≥3500 v/(v h)). In some experiments, O_2 or CO_2 was added to the carrier gas stream. The carrier gas was loaded with halogenated compounds (TeCA, vinyl chloride (VC), trichloroethene (TCE), bromochloromethane (BCM), 1,2-dichloroethane or a mixture of various COCs) by bubbling through spiked silicon oil. The contaminant concentration was ≤1000 ppmv of each. To simulate groundwater strip gas, in most experiments the loaded gas stream was saturated with water at 15 °C. The gas composition was analyzed in each case before and after passing through the reactor, by taking 100 μl gas with a gas-tight syringe from sampling ports and transferring it directly into the GC–MS device.

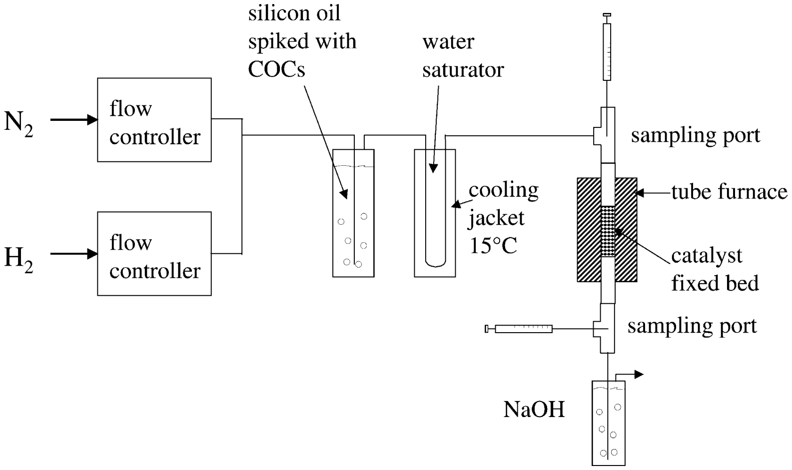

Fig. 1. Scheme of the laboratory device for the gas-phase hydrodehalogenation experiments.

3. Results and discussion

The hydrodechlorination using Pd as a catalyst succeeds quickly and completely for a broad variety of chlorinated compounds with hydrogen as reductant according to $R–Cl+H_2 \rightarrow RH+HCl$ [12,13]. Olefins are completely hydrogenated during the hydrodechlorination reaction under all conditions, whereas the benzene ring usually survives. Cyclohexane was only observed in a few gas-phase experiments with fresh catalyst. In the water phase, the reactions were carried out as batch experiments in the temperature range between 0 and 90 °C. The catalyst was applied in pulverized form to minimize the influence of transport phenomena. Chlorobenzene is completely reduced even at 0 °C with a half-life $\tau_{1/2} \sim 2$–3 min. This is too fast to be kinetically followed with the applied experimental setup and confirms the rapid transport of the reactants to the catalyst sites. The TeCA reduction is much slower than that of chlorobenzene, as shown in Table 1, proving that the TeCA conversion is actually controlled by the rate of the chemical reaction rather than by transport phenomena.

3.1. Hydrodechlorination in water and in the gas phase

The reaction in the aqueous phase follows a first-order kinetics with respect to the COC [3]. The specific catalyst activity A_{Pd} for the dechlorination of TeCA is calculated by Eq. (1)

$$A_{Pd} = \frac{V_{water}}{m_{Pd}\tau_{1/2}} \quad (l/(g\,min)) \tag{1}$$

where V_{water} is the water volume, m_{Pd} the mass of Pd and $\tau_{1/2}$ the compound's half-life, obtained from the disappearance kinetics. It is interesting to compare dechlorination rates for the same COC using the same catalyst (0.5 wt.% Pd on γ-Al_2O_3) in the water phase and in the gas phase.

Fig. 2 shows the temperature dependence of the catalyst activity for the hydrodechlorination of TeCA in the temperature range 0–90 °C. For the gas-phase experiments in the fixed-bed flow-through reactor with hydrogen as carrier gas ($\dot{V}_{gas}$), the catalyst activity (A_{Pd}) was calculated by Eq. (2)

$$A_{Pd} = \frac{\dot{V}_{gas}\ln(c_{TeCA,in}/c_{TeCA,out})}{m_{Pd}\ln 2} \quad (l/(g\,min)) \tag{2}$$

Table 1
Catalytic hydrodechlorination of 1,1,2,2-tetrachloroethane in the water phase (with m_{Pd} = mass of Pd, $\tau_{1/2}$ = half-life, and A_{Pd} = specific Pd activity)

T (°C)	m_{Pd} (mg)	$\tau_{1/2}$ (min)	A_{Pd} (l/(g min))
0	1.350	1700	0.1
15	1.407	490	0.3
25	1.212	330	0.5
50	1.408	50	2.8
70	0.921	40	5.4
90	0.820	25	9.8

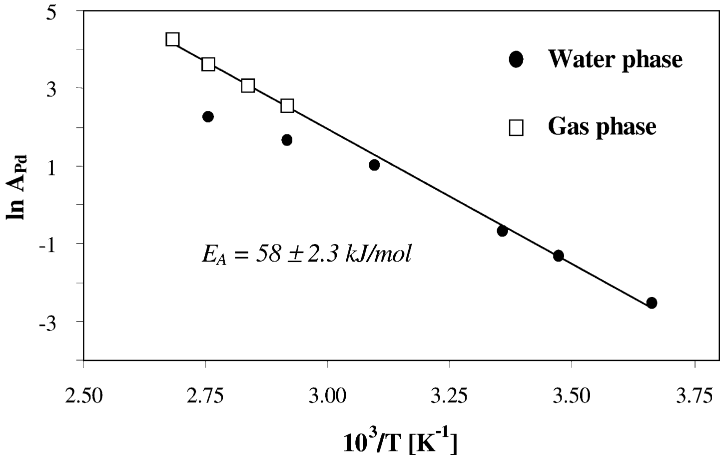

Fig. 2. Temperature dependence of the catalyst activity in the hydrodechlorination reaction of 1,1,2,2-tetrachloroethane using a Pd/γ-Al_2O_3 catalyst in the aqueous and in the gas phase.

It was measured after reaching a steady state of catalyst activity (≥1 h of operation). Apparently, the rate-determining step in the aqueous-phase reaction changes at elevated temperatures, indicated by a curvature of the Arrhenius plot. However, transport limitations of the apparent rates can be ruled out, because unsaturated COCs (such as chlorobenzene) are converted an order of a magnitude faster than TeCA under these conditions. Extrapolation of the catalyst activity from the low-temperature-range water-phase experiments to 100 °C in the moist gas phase, using $E_A = 58$ kJ/mol, leads to the conclusion that the hydrodechlorination of TeCA proceeds at similar rates in both environments (cf. Fig. 2). This is surprising considering the potential role of water for desorption of chloride from the catalyst surface.

Comparing the catalyst performance in the gas phase using water-saturated (15 °C) and dry carrier gas (Table 2), it can be seen that the catalyst was more active in all experiments when using dry H_2. A possible explanation could be that water competes with reactants for catalyst sites rather than it facilitates HCl desorption. Table 2 also shows that the catalyst activity is strongly dependent on its history.

3.2. Selectivity studies

As shown in Fig. 3 with TeCA for example, two principal reaction pathways must be consid-

Table 2

Comparison of 1,1,2,2-tetrachloroethane conversion (X_{TeCA}) using dry and moist carrier gas during a heating and a cooling ramp (0 and 1.7 kPa H_2O, 0.1 kPa TeCA, remainder H_2)

T (°C)	Catalyst heating starting from ambient temperature		Catalyst cooling down after treatment at 150 °C	
	$X_{\mathrm{TeCA,dry}}$ (%)	$X_{\mathrm{TeCA,moist}}$ (%)	$X_{\mathrm{TeCA,dry}}$ (%)	$X_{\mathrm{TeCA,moist}}$ (%)
60	22	15	n.a.[a]	n.a.
70	54	24	75	45
80	70	50	95	66
90	88	62	99	81
100	100	93	100	98

[a] n.a.: not analyzed.

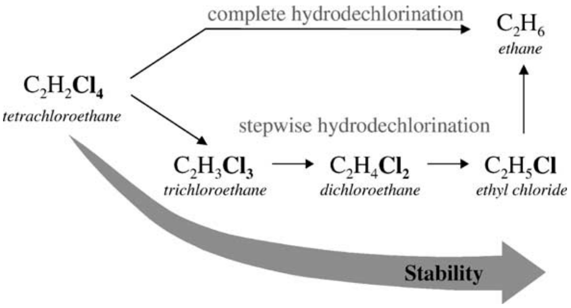

Fig. 3. Reaction pathways for the catalytic dechlorination of 1,1,2,2-tetrachloroethane.

ered when reducing polychlorinated alkanes. Preferably, the COC is reduced directly and completely to the non-chlorinated alkane. If the replacement of chloroatoms occurs in distinct steps, partially chlorinated compounds are formed, which become more resistant to dechlorination when fewer chloroatoms are left in the molecule. The contribution of each reaction pathway to the overall reaction is strongly dependent upon the reaction temperature. The lower the temperature chosen in the gas-phase experiments, the more partially chlorinated compounds were found as relatively stable by-products.

At a temperature of 150 °C, 5% of the converted TeCA was found as by-products, 50° higher only 1% partially chlorinated COCs were detected and at 250 °C only 0.1% by-products left the reactor. Ethyl chloride, the most stable compound in the C_2-family, only starts to be converted at temperatures above 280 °C. This means that although TeCA is already completely converted at lower temperatures, catalyst bed temperatures of at least 250 °C are necessary in order to achieve complete hydrodechlorination. Therefore, for technical application, it is strongly advised to pre-heat the gas stream in order to avoid a temperature drop at the entrance to the catalyst bed, where partial hydrodechlorination could occur.

To simulate a worst-case scenario, an experimental series was carried out with COCs which are significantly more resistant to reduction: dichloromethane (DCM) and 1,2-dichloroethane (DCA). Very high contaminant concentrations between 0.1 and 1 vol.% were chosen here to simulate the enrichment of COCs by vacuum stripping in the pressurized strip gas. The temperature was increased in 50° steps. Neither DCM nor DCA was reduced below the 150 °C temperature step when employed in COC mixtures. At 150 °C, formation of methyl chloride from DCM (about 20% of the 5% of converted DCM) indicates the occurrence of the undesired stepwise dechlorination. The reactivity of COCs in the Pd-catalyzed hydrodechlorination decreases in the order Ph–Cl $\sim$ VC $>$ TCE $>$ TeCA $>>$ DCA $\sim$ DCM. DCA and DCM are not converted with measurable rates ($\tau_{1/2} > 1$ day) in the water phase at ambient temperature. Fortunately, at sufficiently high reaction temperatures (>350 °C) DCA and DCM are also completely reduced. Therefore, catalytic hydrodechlorination in the gas phase offers a universal method for detoxifying all COCs which are otherwise difficult to reduce.

Hydrogenation and hydrodechlorination are competing reactions having chlorinated alkenes as educts. For example, VC is selectively converted to ethane and HCl in an aqueous-phase reaction at ambient temperature at a rate close to the transport limitation (Fig. 4). Applying the same Pd catalyst in the gas phase at 50 °C, VC is rapidly hydrogenated to ethyl chloride, which resists further dechlorination under these conditions. Complete hydrodechlorination of VC can be achieved in the gas phase by increasing the reaction temperature (>190 °C). Obviously, the environment and the choice of the appropriate reaction temperature are essential for controlling the reaction selectivity. The preference of hydrodechlorination in the water phase and at high temperatures in the gas phase can be

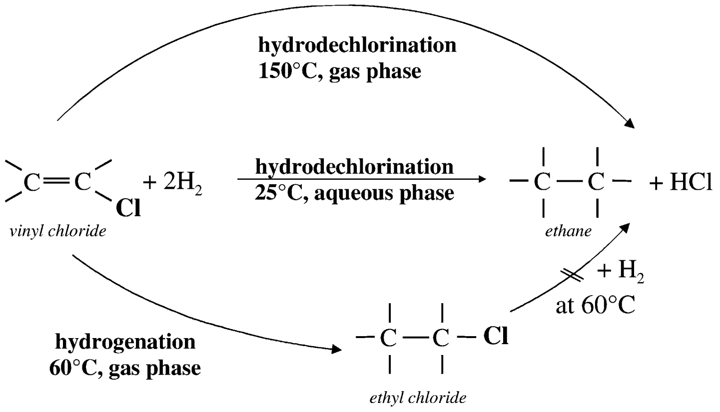

Fig. 4. Reduction pathways of vinyl chloride in the aqueous and in the gas phase.

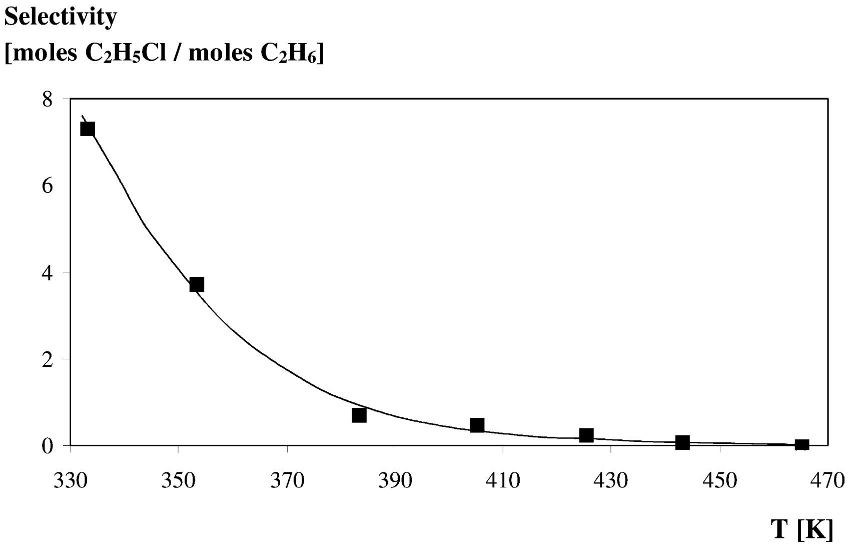

Fig. 5. Competition of hydrodechlorination and hydrogenation in the gas-phase reaction of vinyl chloride, depicted as dechlorination selectivity depending on the temperature.

explained by fast desorption of Cl^- and HCl, respectively, from the catalyst surface as a key step, because chloride at the catalyst surface is known to inhibit the hydrodechlorination, at least in a non-aqueous environment [12–19]. The temperature dependence of the preferred reaction pathway is depicted in Fig. 5.

3.3. Catalyst deactivation/regeneration

Before employing the Pd catalyst under field conditions, it was necessary to study potential problems such as HCl poisoning or HCl erosion of the catalyst carrier, competition of other possible strip-gas components such as CO_2 and O_2 under hydrogen-deficient conditions, and especially sulphur poisoning of the catalyst in the gas phase (from stripped sulphur compounds). After prolonged operation (several days) of the Pd/Al_2O_3 catalyst at moderate temperatures in the gas phase (about 100–150 °C) with COCs in pure hydrogen as carrier gas, a partial deactivation, possibly due to chloride, was observed. Similarly to literature data [15], an increase in the operational temperature (250 °C) ensured a complete restoration of the catalyst activity. To prevent chloride poisoning of the catalyst, the discharge of HCl must be allowed, which we achieved either by choosing a high enough temperature in the gas-phase experiments or by providing a suitable solvating environment, such as water. Other working groups found best results when using bases as proton scavengers [19,20].

When carrying out the gas-phase experiments under H_2 limitation ($p_{H_2} \leq 1$ kPa), a small stoichiometric surplus of hydrogen over the COC content was found to be sufficient to allow the reaction to take place at unreduced rates. Apparently, Pd acts as an efficient hydrogen collector in this pressure range. If the H_2 concentration is further reduced to less than the stoichiometric amount (800 Pa H_2 for 1000 ppmv each of TeCA and TCE), the TCE conversion remains unaffected, whereas the TeCA decomposition reduces. The hydrogen provided is used efficiently; only traces were detected in the exhaust gas leaving the reactor ($p_{H_2,exit} < 50$ Pa).

In order to reduce the expense of groundwater stripping, technical nitrogen or even air may be used instead of high purity nitrogen as strip gases. However, the oxygen thereby supplied is a potential hydrogen consumer and will compete with the COCs for the hydrogen present in the system. In order to study the influence of O_2 on the catalytic hydrodechlorination, the conversion of TeCA and TCE (5000 ppmv each) at 150 °C in nitrogen spiked with air was investigated. Air was injected as a pulse into the headspace above the COC-spiked silicone oil (saturator) and eluted with

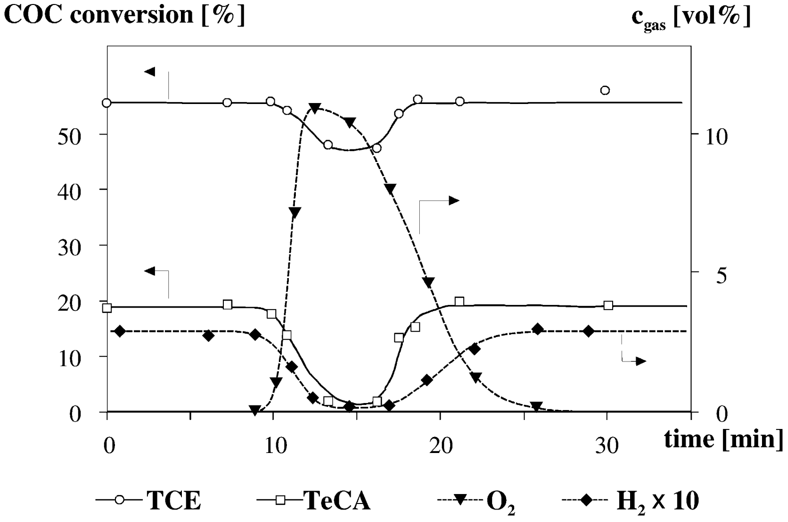

Fig. 6. COC conversion under hydrogen limitation and in the presence of oxygen (oxygen supplied as pulse, $c_{0,\mathrm{TCE}} = c_{0,\mathrm{TeCA}} = 1000\,\mathrm{ppmv}$, $T = 150\,^{\circ}\mathrm{C}$, $c_{0,\mathrm{H_2}} = 5.5\,\mathrm{vol.\%}$, $c_{\mathrm{max,O_2}} = 12\,\mathrm{vol.\%}$, $\dot{V}_{\mathrm{N_2}} = 50\,\mathrm{ml/min}$).

the gas stream. The oxygen pulse was chosen so as to achieve in the peak a maximum of about the four-fold stoichiometric hydrogen demand of the C–Cl bonds to be cleaved. When applying only slightly more than the stoichiometric amount of hydrogen required for the complete hydrodechlorination (4 kPa), COC conversion appeared to remain almost undisturbed. When hydrogen was supplied in excess (>5 kPa), even relatively high oxygen concentrations ($\leq$5 kPa) were tolerated by the system. Fig. 6 shows typical conversion profiles for TCE, TeCA, O_2 and H_2 at the reactor exit when the hydrogen concentration in the strip gas (2 kPa) was limited to about 50% of the stoichiometric demand required for total COC hydrodechlorination (+hydrogenation of the olefin). The TCE conversion is affected only slightly when oxygen is supplied, whereas the TeCA conversion reduces drastically when the oxygen peak reaches its maximum. This means that under hydrogen deficit conditions, the hydrodechlorination of the saturated component, TeCA, can hardly compete with the combination of oxygen and hydrogen at the catalyst surface. In contrast, the dechlorination of unsaturated COCs, such as TCE, occurs without significant inhibition even under these conditions. As a consequence of the kinetic preference of hydrodechlorination, groundwater could be stripped using technical nitrogen or even air as strip gases, provided that hydrogen is present with a sufficiently high partial pressure. In such a case, the reductive dechlorination of COCs (first step) could be combined with a catalytic oxidation of the remaining hydrocarbons (second step), e.g. destruction of benzene formed from chlorobenzene. However, technical nitrogen is the preferred strip gas for removal of aliphatic COCs, because the chlorine-free hydrocarbons (e.g. ethane and methane) do not necessarily require post-treatment. The tolerable oxygen content in the strip gas is dictated by various factors: (i) cost of nitrogen depending on purity, (ii) additional hydrogen consumption, and (iii) tolerable effects in the redox state of the treated water (e.g. iron precipitation).

When stripping water containing carbonate, such as groundwater, carbon dioxide has to be considered as an omnipresent strip-gas component. The above experiments were therefore repeated in the same manner, but replacing oxygen with carbon dioxide. Carbon dioxide did not disturb the hydrodechlorination reactions and was found to be inert in all gas concentrations ($\leq$10 vol.%) and reaction temperatures (100–350 °C) studied.

After extensive laboratory tests, a fixed-bed reactor filled with the same catalyst was installed in a pilot plant for groundwater treatment (1000 l/h) by stripping (3 m^3/h nitrogen) and hydrodechlorination.

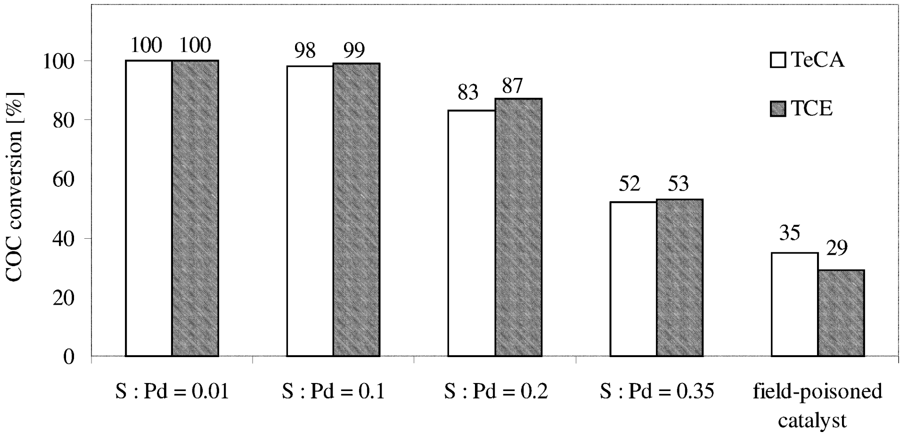

Fig. 7. Conversion of chlorinated hydrocarbons (COCs) depending on the deactivation state of the catalyst ($T = 150\,^{\circ}C$, N_2:H_2 = 10:1; synthetic catalyst poison H_2S; S:Pd given as molar ratios; catalyst after several weeks of field operation).

An essential pre-condition for successful field application is the long-term stability of the catalyst. The major cause of catalyst deactivation is chemical poisoning [21,22] by sulphur compounds, especially H_2S. H_2S and other volatile sulphur compounds, such as dimethyl disulphide, were present in varying concentrations in the groundwater and were stripped together with the COCs. Despite a zinc oxide absorber installed in front of the catalyst, the breakthrough of sulphur compounds could not be completely prevented. As a consequence, a steadily decreasing catalyst activity was observed in the long-term field tests.

The contact of the catalyst with sulphur compounds was simulated in the laboratory experiments by introducing defined amounts of H_2S into the gas stream (Fig. 7). The catalyst showed almost no indication of deactivation when the amount of sulphur introduced was small (S:Pd $\leq$0.1 atom per atom). It must be taken into account here that the S:Pd ratio refers to the amount of H_2S introduced; the fraction of sulphur actually adsorbed was not measured. When more hydrogen sulphide is applied, the conversion of TCE and TeCA is inhibited in the same manner for both compounds. This was unexpected considering the different effects which hydrogen limitation had on the reaction of the two COCs. However, a selectivity shift towards partially chlorinated by-products was observed after the catalyst was exposed to the first traces of sulphur compounds. A fully active, unpoisoned catalyst produced less than 1 mol% by-products at 200 °C, whereas the catalyst with a sulphur dose of S:Pd = 0.2 produced about 10 mol%. The last pair of columns in Fig. 7 show the remaining activity (in the laboratory test) of the catalyst after several weeks of operation under field conditions. During extended operation in the pilot plant, its activity decreased continuously, probably as a consequence of sulphur poisoning not only by hydrogen sulphide but also by volatile organic sulphur compounds. An increase in the operational temperature of the catalyst bed helped to compensate for the steady catalyst deactivation. Nevertheless, after treatment of the field-deactivated catalyst at 200 °C in a H_2 atmosphere in the laboratory reactor for 1 h, its activity remained low. It appears that sulphur poisoning is only partially reversible under moderate reductive conditions. Figoli and Argentiere found a partial regeneration of their supported Pd complexes after sulphur poisoning by conditioning in hydrogen at 80 °C [23]. This raises the questions of whether higher temperatures and a reducing environment would fully regenerate the S-poisoned Pd catalysts or whether the oxidation of the catalyst poisons would lead to success.

Fig. 8 shows the conversion data for TCE and TeCA from the laboratory tests using the field-operated catalyst after various regeneration procedures. As also shown in Fig. 7, operation of the catalyst at 150 °C under test conditions (N_2:H_2 = 10:1) revealed a remaining activity only sufficient to convert about

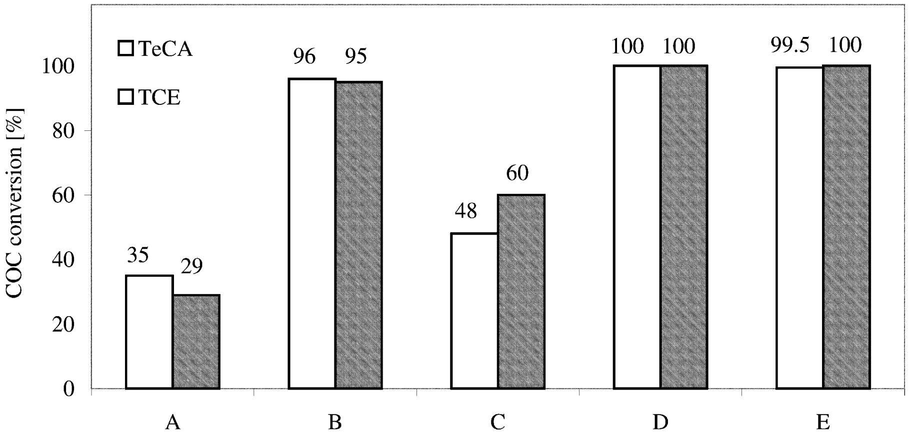

Fig. 8. Conversion of chlorinated hydrocarbons (COCs) after various attempts of regeneration: (A) field-poisoned catalyst without treatment, activity test at 150 °C; (B) catalyst treatment under reducing conditions, activity test at 350 °C; (C) catalyst after treatment B, activity test at 150 °C; (D) oxidative catalyst treatment in air, activity test at 250 °C; (E) catalyst after treatment D, activity test at 150 °C.

one-third of the applied COCs. 30% of the converted COCs were found as by-products in the gas leaving the reactor. The dominant by-products detected were 1,2-dichloroethenes (mainly *cis*-), which were not produced in the experiments using fresh catalyst and H_2S-poisoned samples. An increase in the treatment temperature to 350 °C raised the catalyst activity. However, after setting the test temperature back to 150 °C, the conversion of TCE and TeCA dropped from nearly 100% for both compounds to 48 and 60%, respectively. This means that the catalyst regeneration in a reducing atmosphere was not sustainable.

The catalyst was then exposed to an air stream at increasing temperatures (5 K/min) from 100 to 300 °C. The activity of the catalyst increased continuously with increasing treatment temperature. After reaching 300 °C in the air flow, the catalyst activity was fully restored for the test reaction (N_2:H_2 = 10:1). The full activity still remained after the temperature was set back to 150 °C, i.e. the catalyst could be regenerated by oxidative treatment at elevated temperatures. Interestingly, the partial deactivation leads to a significant shift of the relative hydrodechlorination rates. On the fresh catalyst, unsaturated COCs such as chlorinated ethenes have the highest rate, whereas on the field-deactivated catalyst TeCA is more rapidly dechlorinated. Apparently, saturated and unsaturated COCs react via different mechanisms. Such selectivity and reactivity shifts dependent on the catalyst state have already been reported by other working groups [21,22].

3.4. Hydrodebromination

In addition to chlorinated hydrocarbons, brominated compounds can occur as groundwater contaminants. Therefore, it is interesting to compare the reactivities of C–Cl and C–Br bonds in the Pd-catalyzed hydrodehalogenation reaction. We chose bromochloromethane (BCM) as the probe molecule. It is much more reactive than DCM (at 200 °C, 99% conversion of BCM compared with 10% of DCM). This is consistent with the lower strength of the C–Br bond compared with the C–Cl bond (D^0_{298} = 297 and 350 kJ/mol, for Br–CH_2Br and Cl–CH_2Cl respectively [24]). In the temperature range of 100–200 °C, methane is the major product, but small proportions of methyl chloride and methyl bromide were also found as by-products of the stepwise dehalogenation reaction (Table 3).

The data provide evidence of a significant temperature dependence of the dehalogenation ratio. The preferred substitution of the Br atom at 100 °C is as expected, whereas the preference of the Cl atom at 200 °C is surprising. At even higher temperatures (>250 °C) neither methyl chloride nor methyl bromide were observed. The results obtained with BCM indicate that brominated organic compounds can be

Table 3
Catalytic hydrodehalogenation of bromochloromethane (BCM, $c_0 = 1000$ ppmv, moist H_2 as carrier gas, space velocity 3500 v/(v h))

T (°C)	X_{BCM} (%)	CH_3Cl (as mol% of converted BCM)	CH_3Br (as mol% of converted BCM)
100	10	30	<1
150	90	3	1.5
200	99	0.5	2.5

degraded in a similar manner to COCs with Pd-based catalysts.

4. Conclusions

The present paper shows that a commercially available Pd/Al_2O_3 catalyst is suitable for hydrodechlorination of chlorohydrocarbons stripped from a complex contaminated groundwater containing considerable amounts of volatile sulphur compounds. The catalyst history and the reaction temperature determine the catalyst's activity and selectivity. Deactivated catalysts can be efficiently regenerated by oxidative treatment at elevated temperature, whereas regeneration in a reductive environment is not sustainable. Catalysts partially deactivated after their utilization in the field show a selectivity shift: on fresh catalyst, chloroethenes react with higher rates, whereas on partially poisoned catalyst, the saturated compound 1,1,2,2-tetrachloroethane was more rapidly dechlorinated. Applying bromochloromethane as probe molecule, it has been shown that brominated organic compounds can be degraded similarly but preferred to their chlorinated pendants using Pd-based catalysts.

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References

[1] W.W. McNab, R. Ruiz, Chemosphere 37 (1998) 925.
[2] C. Schueth, M. Reinhard, Appl. Catal. B 18 (1998) 215.
[3] C. Schueth, S. Disser, F. Schueth, M. Reinhard, Appl. Catal. B 28 (2000) 147.
[4] L. Prati, M. Rossi, Appl. Catal. B 23 (1999) 135.
[5] B. Coq, F. Figueras, J. Mol. Catal. A 173 (2001) 117–134.
[6] K. Pirkanniemi, M. Sillanpää, Chemosphere 48 (2002) 1047.
[7] N.E. Korte, J.L. Zutman, R.M. Schlosser, L. Liang, B. Gu, Q. Fernando, Waste Manage. 20 (2000) 687.
[8] K. Mackenzie, R. Koehler, H. Weiss, F.-D. Kopinke, in: G.B. Wickramanayake, A.R. Gavaskar, A.S.C. Chen (Eds.), Chemical Oxidation and Reactive Barriers: Remediation of Chlorinated and Recalcitrant Compounds. Battelle Press, Columbus (Richland), 2000, p. 331.
[9] F.-D. Kopinke, R. Koehler, K. Mackenzie, C. Schueth, Grundwasser 3 (2002) 140.
[10] G. Centi, J. Mol. Catal. A 173 (2001) 287.
[11] J. Staudinger, P.V. Roberts, Crit. Rev. Environ. Sci. Technol. 26 (1996) 205.
[12] F.J. Urbano, J.M. Marinas, J. Mol. Catal. A 173 (2001) 329.
[13] B. Coq, G. Ferrat, F. Figueras, J. Catal. 101 (1986) 434.
[14] G. Del Angel, J.L. Benitez, J. Mol. Catal. A 165 (2001) 9.
[15] J.L. Benitez, G. Del Angel, React. Kinet. Catal. Lett. 70 (2000) 67.
[16] P. Forni, L. Prati, M. Rossi, Appl. Catal. B 14 (1997) 49.
[17] M.A. Aramendia, V. Borau, I.M. Garcia, C. Jimenez, F. Lafont, A. Marinas, J.M. Marinas, F.J. Urbano, J. Mol. Catal. A 3517 (2002) 1.
[18] M.A. Aramendia, V. Borau, I.M. Garcia, C. Jimenez, F. Lafont, A. Marinas, J.M. Marinas, F.J. Urbano, J. Cat. 187 (1999) 392.
[19] M.A. Aramendia, V. Borau, I.M. Garcia, C. Jimenez, J.M. Marinas, F.J. Urbano, Appl. Catal. B 20 (1999) 101.
[20] E.N. Balko, E. Przybylski, F. Vontrentini, Appl. Catal. B 2 (1993) 1.
[21] P. Albers, J. Pietsch, S.F. Parker, J. Mol. Catal. A 173 (2001) 275.
[22] J.C. Rodriguez, J. Santamaria, A. Monzon, Appl. Catal A 165 (1997) 147.
[23] N.S. Figoli, P.C.L. Argentiere, J. Mol. Catal. A 122 (1997) 141.
[24] D.R. Lide, Handbook of Chemistry and Physics, 76th ed., CRC Press, Boca Raton, 1996, pp. 9–66.