Thermal conversion of hydrocarbons on solid matrices

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Abstract

The paper examines the influence of organic and inorganic matrices of different structure and origin on the thermal conversion of hydrocarbons such as polycyclic hydrocarbons (PAHs) and alkanes to non-volatile products (process known as "charring"). Independence on the solid-structure different reaction pathways are discussed. The charring activity was measured as a function of matrix type and activation temperature. The activity of sediment ash as a special inorganic matrix is caused by reasons other than high surface area and acidic centres. In this case a redox behaviour was observed.

1. Introduction

The thermal cleanup of organically contaminated solids has become a topic of interest. Low-temperature thermal treatment processes (LTTP, $T \leq 300°C$) play an important role among the so-called innovative technologies specially designed for soil remediation [1,2]. Several technologies are available for soil cleaning by thermodesorption. One of the most frequently used reactors is the rotary kiln. Other extreme technologies with respect to heating rate and residence time include the fluidized bed reactor and the in situ radio-frequency heating of contaminated soil; the latter needs no reactor [3–6]. During these thermodesorption processes volatile compounds can evaporate from the contaminated materials as the desired result [7–9]. Furthermore, semivolatile compounds found to be at least partially removed [10,11], indicate chemical conversion either by pyrolysis, hydrolysis and/or by oxidation taking place during the thermal treatment. Besides volatile fragments, another portion of the target compounds can produce bound residues, co-

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valently attached to the soil organic matter (SOM). The process producing bound residues is called charring [12–15]. As the result of this process, organic pollutants become a part of the polymer network. That means the backbone of the pollutants need not be destroyed.

We have published results about reactions of hydrocarbons during thermodesorption from sediments [16]. The experiments on thermally and oxidatively pretreated sediment fractions have shown that there is no common correlation between the amount of organic matter (OM) in the differently treated solids and their charring activity. No significant activity increased after a wet oxidation was found (H_2O_2/KOH, remaining content of OM about 2 wt%) compared to the original sediment (16 wt% OM). The thermal pretreatment under an inert atmosphere (N_2, 300°C, 1 h) diminished the amount of OM to a lower extent than the wet oxidation, but surprisingly raised the catalytic activity in the PAH conversion significantly. However, the value of the charring activity is lower than that known for air activated samples. No clear distinction between the contribution of the organic and the inorganic components of the sediment to the PAH conversion can easily be made on the basis of these experimental data. The experiments indicate that oxidation increases the catalytic activity of the matrices studied, although an influence of SOM can only be excluded in the case of the SOM-free sediment ash. One of the conclusions in a recent paper [16] was that sediment ash is more active in hydrocarbon conversion reactions than the original sediment. This points to the mineral matrix of the sediment, rather than the SOM, as the actual carrier of the catalytic activity.

Therefore, the present paper deals with the influence of different inorganic matrices as well as some natural polymers, such as cellulose and humic acids, on the charring process.

2. Experimental

The sorbate compounds were commercially available and used without purification (purity >98%, see also Table 3). The sediment ash samples were prepared by burning a sediment sample taken from the river Weisse Elster near the city of Leipzig at 550 and 900°C for 1 h. The clay catalyst KS and the fly ashes (from the lignite power plants Neurath, Jänschwalde and Thierbach) were supplied by Süd-Chemie AG and by VEAG-Vereinigte Energiewerke AG, respectively. The γ-Al_2O_3 catalyst was available from Leuna-AG (type 5800) (for properties determined, see Table 1). The other materials used and their origins were as follows: molecular sieve MS13X (Chemie-AG Bitterfeld), humic acid (Aldrich), cellulose (Aldrich) and zinc chloride (Merck). Both the inorganic matrices and the organic materials were dried and sieved to obtain size fractions <63 μm. The loading of sorbents with the sorbate compounds was 500 ppm per component except chrysene (250 ppm) in all cases.

The impregnation of the sorbents with sorbate compounds and other experimental details are described in Ref. [16]. About 20 mg of impregnated sorbents were pyrolysed in a sealed glass capillary (50 × 1.6 × 0.16 mm³) put into a copper tube at 300°C for a period of 1 h in a muffle furnace (±5°C). After cooling, the samples were checked for tightness by weighing. The treated samples were then extracted under flow conditions in

Table 1

Selected properties of inorganic matrices

Inorganic matrix	Surface area/(m^2 g^{-1})	pH value (10 wt% water suspension)	Organic carbon/wt%
Fly ash 1	1.4	12.5	0.44
Fly ash 2	1.5	12.5	0.13
Fly ash 3	14.8	12.7	1.79
KS[a]	280	2.5[c]	n.d.
γ-Al$_2$O$_3$[b]	265	7.5	<0.1
Zeolite	n.d.	7.5	<0.1
Sediment ash (550°C)	14	9.8[c]	<0.1

[a] Acid-activated clay catalyst (Ca-bentonite).
[b] Catalyst type 5800.
[c] Burned at 900°C.

an ultrasonic bath with 0.5 ml of a benzene–acetone mixture (1:1) within about 10 min. After adding n-heptadecane as an internal standard, the collected extract was analysed by GC without performing any cleanup. The GC conditions were as follows: 50 m capillary column NB 54 coated with 5% phenyl- and 1% vinylsilicone gum, 0.32 mm i.d., film thickness 0.25 μm. The oven temperature was programmed from 40 (initial time 10 min) to 285°C (final time 30 min) with a heating rate of 4 K min^{-1}, carrier gas He, split 1:75, FID. In both cases the detector and injector block was set to 280°C. For data handling an APEX®-chromatography workstation was used. The recovery rates, based on GC analysis of the hydrocarbons from blank experiments (impregnation and extraction without thermal treatment), were in the range 90–100%. The thermogravimetric analyses were performed with a thermobalance (TGA-50, Shimadzu Corp.) under a helium atmosphere.

3. Results and discussion

Following our earlier experiments which investigated the different activity of sediment ash and the original sediment in hydrocarbon conversion reactions [16], we studied first the contribution of organic matter to the charring process. Furthermore, we were interested in the influence of zinc chloride as a well-known charring agent [15,17] in the presence and absence of different organic matrices, as well as the influence on different inorganic solids, such as fly ashes and other potential catalysts for hydrocarbon conversion.

In order to determine to what extent the organic parts of the solid matter participate in the conversion reactions we prepared mixtures of an inert inorganic material and different organic matrices. Quartz sand as carrier produced low conversion degrees even after 16 h of pyrolysis at 300°C [16]. Biopolymers such as humic acid, cellulose and hemicellulose were diluted with quartz sand in the ratio 1:1. This mixture was loaded with the hydrocarbons under study and pyrolysed at 300°C for 1 or 4 h in sealed glass capillaries.

Table 2

Conversion of hydrocarbons sorbed on biopolymers diluted with quartz sand (1:1) in sealed capillaries at 300°C in %

Biopolymer	Hemicellulose	Cellulose	Humic acid	Humic acid (Na-salt)
Time of reaction/h	1	4	4	4
n-Dodecane	<5	<5	<5	<5
Methylnaphthalenes	16	<5	<5	<5
Diphenyl	27	<5	<5	<5
Acenaphthene	47	60	50	45
n-Hexadecane	<5	<5	<5	<5
Fluorene	52	60	80	45
Phenanthrene	39	15	28	<5
Anthracene	52	40	36	<5
2-Methylphenanthrene	44	25	34	<5
n-Eicosane	<5	<5	<5	<5
9-Methylanthracene	55	39	45	<5
Fluoranthene	52	23	25	<5
Pyrene	59	35	21	<5
p-Terphenyl	41	<5	<5	<5
Chrysene	60	<5	<5	<5

The mixture used for thermal treatment experiments contained 14 PAHs and three n-alkanes. Table 2 presents the recovery rates after the thermal treatment of these mixed matrices. Conversion degrees below 5% were not taken into account.

The organic solids diluted with quartz sand to the same extent show a different reactivity in their PAH consumption. Hemicellulose as a thermolabile biopolymer allows a conversion for all PAHs introduced. However, the sodium salt of humic acid, having a higher stability [18], does not effect a significant conversion of most of the PAHs even after a reaction time of 4 h. Cellulose and pure humic acid are comparable in reactivity, whereby considerable conversions of 2- and 3-ring membered aromatics were found. Surprisingly, the experimental data give no clear picture with a view to the reaction mechanism, because in the case of hemicellulose as reactive matrix even very stable PAHs such as diphenyl and p-terphenyl are also converted. Reaction patterns typical of kinetically controlled radical reactions were not observed. For PAHs with different structure and reactivity, different consumption degrees were expected. In contrast to this assumption, we found a similar conversion of the chemically reactive 9-methyl-anthracene and the much more stable p-terphenyl. These findings point to overlapping effects of volatility and reactivity as factors, which control the conversion of the PAHs. A possible interpretation of these experimental results could be an initial sorption of the aromatic hydrocarbons followed by a poorly selective conversion at the coke matrix, which is formed by dehydration and decarboxylation of the thermally treated biopolymer. A rough estimation of vapour pressures and the dead volume inside the sealed capillaries shows that all the PAHs up to chrysene could be completely vaporized unless they are adsorbed on the solid organic matter. The gas phase reaction of PAHs is too slow to produce a significant consumption [19]. Therefore, the adsorption-desorption equilibrium

Table 3

Conversion of some PAHs on various fly ashes and on sediment ash pretreated in air at 900°C (300°C, 1 h) in %

	Fly ash 1 (Neurath)	Fly ash 3 (Jänschwalde)	Fly ash 3 (Thierbach)	Sediment ash
Acenaphthene	74	48	46	21
Fluorene	68	34	31	19
2-Methylphenanthrene	15	8	12	<5
9-Methylanthracene	58	31	33	29

Compounds not listed produce no significant reaction

can be decisive for their consumption. The main conclusion of these studies is that organic matrices are in principle able to convert semivolatile PAHs into non-volatile substances or coke (captive organic matter). However, this effect is not as pronounced as that known for the oxidatively activated sediment.

In order to investigate the influence of the inorganic matrix, some solids with different structures and origins were studied. In further experiments the charring activities of fly ashes from lignite power plants and sediment ash heated up to 900°C (1 h) were determined. Table 3 presents the results of charring experiments under standard conditions.

Only the most reactive PAHs (acenaphthene, fluorene, 2-methylphenanthrene and 9-methylanthracene) with a structure–count ratio [20,21] ≥3 are significantly consumed after a reaction time of 1 h. Neither the fly ashes nor the thermally treated sediment ash sample show a significant catalytic activity for conversion reactions of most of the PAHs. Possible reasons for this finding are: the loss of catalytic activity of the mineral matrix as result of the high temperatures during the ash formation or post-treatment; the low surface area; and the lack of acidic centres.

Several mineral materials were tested for their charring activity to answer the question of which kinds of active centres are responsible for the increased conversion of PAHs on sediment ash produced at 550°C. The matrices chosen for this experiment are rich in acidic centres and have a high specific surface, e.g. acid activated clay (catalyst type KS), γ-alumina (catalyst type 5800) and the synthetic zeolite MS13X (see Table 1). The inorganic matrices described were heated in air at 550°C for 1 h in a muffle furnace, analogous to the procedure for the sediment. The results of the charring experiments are listed in Table 4.

It is well known from the literature that mineral materials (e.g. calcite, kaolinite, pyrite) are able to catalyze isomerization, aromatization and cracking reactions of hydrocarbons at higher temperatures [22,23]. Under mild conditions dimerization, isomerization, condensation and redox reactions take priority; at higher temperatures especially the cracking, aromatization and dehydrogenation reactions are catalyzed by active minerals.

The acid activated catalyst KS converts PAHs nearly quantitatively and higher n-alkanes partially at 300°C and 1 h reaction time. Furthermore, we can state that n-paraffins remain unaffected on MS13X in contrast to acid-activated clay matrices. This experimental result indicates that an acid activation of mineral material enhances its

Table 4

Conversion of hydrocarbons on selected mineral catalysts and in the presence of zinc chloride (300 °C, 1 h) in %

	KS	γ-Al$_2$O$_3$	MS13X	Quartz sand + zinc chloride	Cellulose + zinc chloride	Sediment ash [16]
n-Dodecane	<5	<5	<5	<5	<5	<5
Naphthalene	98	<5	87	91	87	12
Methylnaphthalenes	>99	<5	81	84	81	50
Diphenyl	84	<5	87	77	87	10
Acenaphthene	>99	<5	>99	>99	>99	>99
n-Hexadecane	25	<5	<5	<5	<5	12
Fluorene	>99	<5	94	>99	94	>99
Phenanthrene	>99	<5	91	95	91	42
Anthracene	>99	32	96	>99	96	95
2-Methylphenanthrene	>99	<5	90	>99	90	83
n-Eicosane	36	<5	<5	<5	<5	29
9-Methylanthracene	>99	30	87	>99	87	>99
Fluoranthene	>99	<5	>99	>99	>99	96
Pyrene	92	<5	>99	>99	>99	65
p-Terphenyl	86	<5	88	82	88	34
Chrysene	89	(20)	94	86	94	69

catalytic activity for the conversion of the relatively inert paraffins. The activity of γ-alumina under the chosen experimental conditions is surprisingly low, even lower than that of the fly ashes tested. Apparently, a high specific surface is not a determining condition for a high charring activity of a mineral matrix. Density and distribution of the acidic centres seem to play the more important role in this process.

It is known from the literature that the addition of the strong Lewis acid zinc chloride to biopolymers diminishes the decomposition temperature and raises the tendency for coke formation by extensive acid catalyzed dehydration and condensation reactions [15]. To study the influence of ZnCl$_2$ on the activity of matrices, quartz sand and cellulose were both treated with a 25% aqueous solution of ZnCl$_2$ (1 ml ZnCl$_2$ solution to impregnate 1 g matrix followed by drying at 105°C) and loaded with the sorbate mixture. These solids were heated for 1 h at 300°C in the same manner as comparable samples.

Table 4 (columns 4 and 5) shows that the addition of ZnCl$_2$ to quartz sand as well as to cellulose increases the PAH-conversion rate on those matrices. However, n-alkanes do not react. The PAH-conversion on ZnCl$_2$-doped quartz sand is even higher than on cellulose. Compared to cellulose the aromatic hydrocarbons are pure and in low concentration on the quartz surface. The PAHs are in direct contact with the high excess of added ZnCl$_2$, which allows an acidically catalyzed condensation to higher molecular weight units without the influence of an organic polymer matrix. In contrast to the above, cellulose itself forms a coke matrix in the presence of ZnCl$_2$ by dehydration and condensation reactions of unsaturated pyrolysis products. Consequently, PAHs can be bound covalently either by radical addition reactions or acidically catalyzed condensation.

As was shown in the previous studies of various matrices, the high charring activities

of the sediment ash cannot be explained sufficiently by a high specific surface or by the presence of acidic centres at a temperature of 300°C. The explanation may be found in the composition of the inorganic part of the sediment, which (according to X-ray fluorescence analysis) consists of 75 wt% SiO_2, 12 wt% Al_2O_3 and several heavy metals. The most significant are iron (5.5 wt%), zinc (2800 ppm), manganese (940 ppm) and chromium (640 ppm). These heavy metals can occur in different oxidation states. According to our hypothesis, heavy metals as well as other inorganic sediment components may be oxidized in air at 550°C and can therefore become oxidizing agents themselves, which may be responsible for PAH conversion reactions. The redox behaviour of the inorganic matrices should be reversible. This is confirmed by deactivated sediment ash samples which could be reactivated by additional oxidative treatment.

Attempts to reduce ash in a hydrogen atmosphere support this view. Up to 300°C we found no loss of activity of the sediment ash by hydrogen treatment. Sediment ash is reducible in hydrogen above 330°C. The ash loses approximately 1.6 wt% during reduction up to 600°C. This finding indicates oxidic rather than peroxidic structures for the sediment matrix, which may induce the oxidation of supported PAHs.

The redox behaviour of sediment ash doped with 1 wt% 9-methylanthracene (9-MA) was studied using a thermobalance (see Fig. 1). 9-MA, impregnated on sediment ash (550°C), is converted quantitatively to higher molecular weight products (ca. 65 wt%) and coke (ca. 35 wt%), not shown in Fig. 1. A reduction of the same sample with hydrogen after burn-off at 600°C was complete after 20 min, with a weight loss of ca. 1.3 wt%.
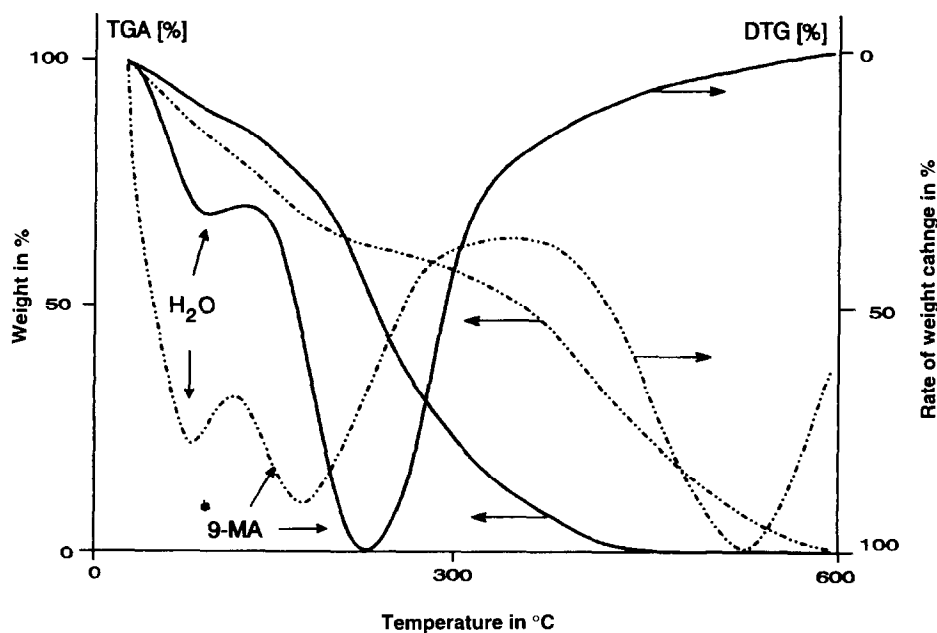

Fig. 1. Redox behaviour of sediment ash doped with 9-MA. Solid line, reduced sample (second run); dotted line, oxidized sample (third run).

The reduced sample was loaded with 9-MA at room temperature and heated up to 600°C in a second run under an inert atmosphere ($\dot{T}$ = 10 K min^{-1}). The 9-MA could be desorbed with a yield of more than 85% yield. The coke yield, determined by burn-off, was found to be only 4 %. This indicates that the catalytic activity of the sediment ash is markedly diminished by reduction with hydrogen. In a third run the same sample, reactivated in air at 550°C, was loaded a third time with 9-MA and heated to 600°C. Of the 9-MA introduced, 20% was desorbed up to 300°C, 60% was converted into higher molecular weight products and the remaining 20% formed a coke residue. These experimental results suggest a reversible redox process as the controlling step in the PAH conversion.

Similar observations with respect to the redox behaviour of mineral matrices have been made with calcium aluminates [24], which are used as catalysts for olefin production. It is not yet known which parts of calcium aluminates are the reactive centres. Ozonides and radical Al–O structures (so-called "oxygen hole centres") have been suggested. They could be of importance for radical formation from hydrocarbons [25].

It is now understandable that the native sediment has a lower charring potential for PAHs than the sediment ash formed at 550°C. The most active centres for a PAH conversion are generated during air treatment. The oxygen introduced into the mineral matrix is available for oxidation reactions of hydrocarbons at elevated temperatures. It may initiate further radical reactions of PAHs, giving rise to non-volatile condensations products.

This view can explain the observed selectivity of conversion of PAHs on sediment ash [16], which is in conformity with their reactivity in radical reactions.

Conclusions

This paper presents results about the conversion of hydrocarbons such as PAHs and paraffins during a low-temperature thermal treatment (LTTP, ≤300°C) on various organic and inorganic matrices. The processes may play an important role in thermodesorption of hydrocarbons from polluted soils or other solid materials. Until now, the thermodesorption process has mainly fallen into the responsibility of engineers rather than chemists. That means, the evaporation of volatile compounds has been assumed as controlled by sorption equilibria, mass transfer and mass transport phenomena. Soils and the pollutants were assumed to be chemically inert and chemical reactions are not considered. In this paper we give evidence that organic matter is able to convert semivolatile hydrocarbons into non-volatile products and coke, when heated up to about 300°C. However, this effect is not as pronounced as observed for acid activated clay, $ZnCl_2$-doped solids and an oxidatively activated sediment. In the case of the sediment ash, centres providing reactive oxygen are generated during the oxidative pretreatment. Oxygen, introduced into the mineral sediment matrix, is able to act as an oxidizing agent and, therefore, to initiate oxidation reactions at elevated temperatures. This process was found to be reversible, suggesting a redox behaviour of the mineral matrix.

In consequence, biopolymers as well as mineral matrices can stimulate chemically the conversion of pollutants during thermodesorption. The presence of active oxygen may supports the charring process of semivolatile compounds.

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