

Degradation of Organic Compounds on Fly Ash: Investigating the Role of the Support

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1. Introduction

Since the detection of polychlorinated dibenzodioxins, PCDDs, and polychlorinated dibenzofurans, PCDFs, in the emissions of Municipal Solid Waste, MSW, incinerators, the formation and degradation reactions of these compounds have been intensively studied¹⁾.

Aim of our research is the study of the degradation and formation reactions of most organic compound on fly ash. A kinetic study of this type requires a tremendous analytical effort. Such a study, even if feasible, is practically impossible, taking a too long time to be completed. On the other hand, the global study has great importance particularly for its practical implications in the treatment and disposal of fly ash.

The solution we are proposing is to study the behavior of organic compounds on fly ash through a global parameter. Of course, specificity will partly be lost, since the model we obtain does not describe in an exact manner the behavior of every compound taken separately. Nevertheless, it is very useful for practical purposes.

As global parameter we have chosen the Total Organic Carbon²⁾ (TOC) content, used to measure the reagents' concentrations.

Experiments are performed on fly ash from MSW incinerators and, to help in the interpretation of the results, on synthetic mixtures of pure compounds on silica gel, SiO₂, as a model support.

In a preliminary study³⁾ we reported the results of batch experiments on fly ash from MSW incinerators and synthetic mixtures of dibenzofuran, DF, biphenyl, BPh, and activated carbon. In the runs on model systems any catalyst or chlorine source are added to the support. Data for the runs on synthetic mixtures were fitted with a first-order kinetic equation. For the runs on fly ash a mechanism of two simultaneous independent first-order reactions, R1 and R2, was hypothesized and the data were fitted with an iterative procedure. The results led to the conclusion that processes both on the model support and on fly ash are diffusion controlled.

In the present study we report about further experiments performed to a) determine the *reaction products*, and b) confirm the *role of the support* in the diffusion control.

2. Experimental and results

Details of the reagents and materials used and of the experimental procedure for the kinetic studies have been already reported³⁾.

a) *Reaction Products*. To identify the reaction products, thermal treatments of the pure DF and activated carbon, of the synthetic mixtures and of untreated fly ash are performed in a closed tube using a set-up represented in Figure 1. Samples were treated in closed tube for 2 h; after the treatment, nitrogen (100 ml/min) flows through the tube for 1 h, bubbling in a series of five impingers, the first filled with cyclohexane, the following four with a saturated Ba(OH)₂ solution. Preliminary experiments showed that one impinger filled with cyclohexane and four impingers filled with saturated Ba(OH)₂ solution are sufficient to collect the organics and the carbon dioxide developed in the reaction conditions.

EMCO

dioxide developed in the reaction, the four Ba(OH)₂ solutions and a blank are titrated with HCl 0.5 N. The residual TOC content of the sample is determined.

Table 1 shows the distribution of the products in the different reactions. For DF, both as a pure compound or in a mixture with SiO₂, the only product is the reactant, recovered in the organic solvent. For activated carbon, a single product is found, carbon dioxide. For the reactions of fly ash at 250°C and 325°C, CO₂ is the main product; tetra- to hexachlorobenzenes have been detected in the impinger with the organic solvent, but until now not quantified. At higher temperatures (500°C), CO₂ is the only product.

Table 1. Products of the thermal treatment of pure compounds, synthetic mixtures thereof or fly ash in closed tube at different temperatures^a.

sample	T (°C)	TOC(t=0)	TOC(t=2h) (%)	CO ₂ (%)	Organics (%)	Recovery %
DF	75	9 10 ⁵	-	-	99	99
DF/SiO ₂	56	3770	100	-	1 ^b	101
DF/SiO ₂	75	5890	95	-	17 ^b	112
DF/SiO ₂	150	3770	45	-	44 ^b	89
C	400	10 ⁶	44	48	-	92
C/SiO ₂	350	1350	91	18	-	109
C/SiO ₂	400	1350	67	44	-	111
C/SiO ₂	550	1350	0	100	-	100
fly-ash	250	4790	71	15	(c)	92
fly-ash	325	4790	69	10	(c)	79
fly-ash	500	4790	6	94	-	100

(a) Reaction product data are given in % of the initial TOC.

(b) Organics = DF

(c) Tetra- to hexachlorobenzenes were detected, but not quantified.

b) Role of the Support. In order to gain information on the role of the support, the behavior of pure DF and activated carbon was also studied. The reaction temperature ranged from 57 to 150°C for pure DF, from 325 to 600°C for pure activated carbon; the reaction times varied from 15 to 240 minutes. The results are reported in Tables 2 and 3. The data for the runs on the pure compounds were fitted with a first-order kinetic equation. The rate constants (min⁻¹) are shown in Figure 2a-b, as Arrhenius plots together with the Arrhenius plots obtained for the reaction of the SiO₂-mixture of the compounds³. Table 4 reports the activation parameters.

3. Discussion and Conclusions

DF undergoes a physical transformation from solid to gaseous state (Table 1) according to a pseudo-first order kinetic. For activated carbon, the reaction is a combustion to gaseous CO₂ (Table 1) following a pseudo-first order kinetic.

Looking at the Arrhenius plots (Figure 2), a linear trend is observed for pure DF and activated carbon reactions, while a non-linear trend, depicted as two connected straight lines with different slopes, is observed for the synthetic mixtures reactions. To explain this behavior, we hypothesize a physical and/or chemical adsorption of DF or carbon on the surface and in the pores of SiO₂. At lower temperatures, the rate-limiting step is the desorption of DF from the surface or the combustion of carbon to CO₂. At higher temperatures, the rate-limiting step is the diffusion of DF or CO₂ through the pores of the

support.

On the basis of this hypothesis and according to the calculated activation parameters (Table 4) for fly ash, both reactions R1 and R2 are confirmed to be diffusion controlled. One of the two reaction, probably R1 having the higher apparent activation energy, could correspond to the carbon oxidation to CO₂; the other could be a desorption of polychlorobenzenes.

Results obtained for the SiO₂ mixtures point out the important role of the support in determining kinetics and mechanism of these reactions. This hypothesis will be further tested: other batch experiments with different starting carbon content and runs on a continuous flow apparatus are needed.

Table 2. Thermal treatment of pure DF: DF (mg) - time data at different temperatures.

t(min) T(°C)	0	15	30	60	90	120	150	180	210	240
57	368		330	321	256	217	196	183	164	134
68	102			70		45		25		8
75	304		236	160	146	122	86	86	47	36
87	100		59	44		10		4		
100	110		33	20	6					
125	100	26	2							
150	112	18								

Table 3. Thermal treatment of pure activated carbon: C (mg) - time data at different temperatures.

t(min) T(°C)	0	15	30	60	90	120	150	180	210	240
325	98		92	87	86	76	69	69	66	64
350	201			154		144		110		83
375	101		83	64	56	45	36	30	21	17
500	99		14	2						
600	250	21	2							

Table 4. Activation parameters: ΔE^\ddagger (kcal mol⁻¹) and ln A.

	DF-SiO ₂ ³⁾		pure DF 57-150°C	C-SiO ₂ ³⁾		pure C 325-600°C	Fly Ash ³⁾	
	50-75°C	75-200°C		325-375°C	375-600°C		R1	R2
ΔE^\ddagger	23.58	5.947	11.89	59.98	7.884	16.89	6.780	3.240
lnA	23.2	-2.07	12.7	36.6	-4.19	8.03	-5.78	-5.77

5. References

- 1) For a short review of general references, see: Lasagni M., G. Moro, D. Pitea, and L. Stieglitz (1991): *Chemosphere* 23, 1245-53
- 2) Lasagni M., E. Collina, M. Tettamanti, M. Ferri, and D. Pitea (1993): *Organohalogen Compounds* 11, 199-202
- 3) Collina E., M. Lasagni, M. Tettamanti, M. Mapelli, L. Forni, and D. Pitea (1993): *Organohalogen Compounds* 11, 265-268

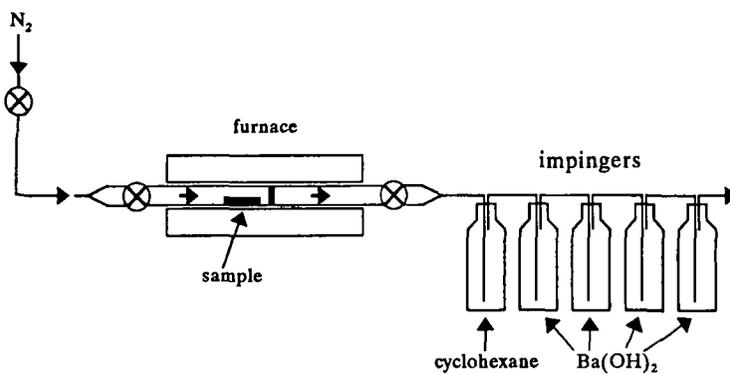


Figure 1. Apparatus for the identification of the products.

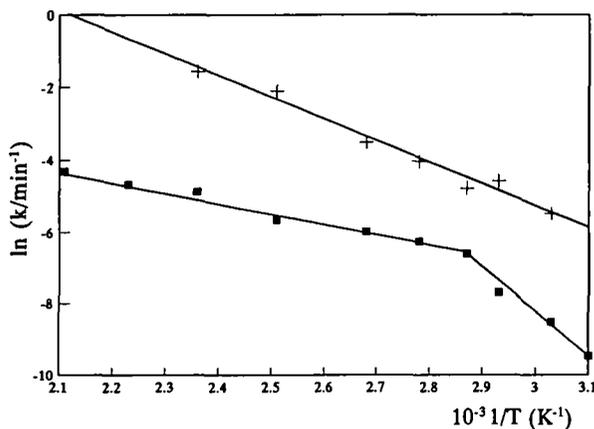


Figure 2a. Arrhenius plots for the reactions of pure DF (+) and DF-SiO₂ mixture³⁾ (■)

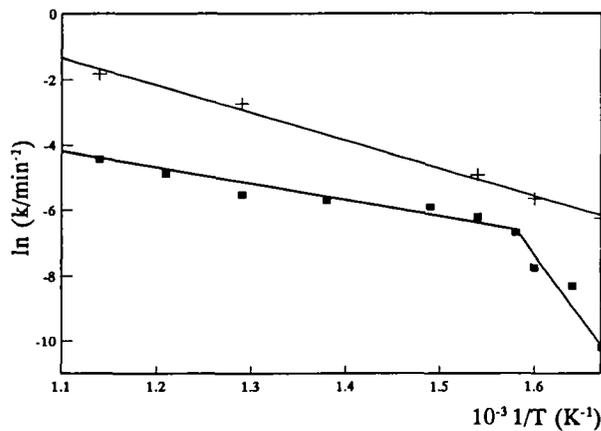


Figure 2b. Arrhenius plots for the reactions of pure Carbon (+) and C-SiO₂³⁾ mixture (■)