Fly Ash as Catalyst for Dimerisation of Toluene

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ABSTRACT

Dehydrodimerisation of toluene and the oxidation to benzaldehyde and benzyl alcohol are the most favoured reactions at low temperatures (298-383K). These reactions are catalysed by the metal oxides being found on fly ash.

INTRODUCTION

The reaction mechanisms leading to PCAHs especially the PCDDs/PCDFs in the presence of fly ash are doubtless of major interest. These substances are of special relevance because of their toxicology and emission during incineration processes.

There are still other reactions of organics on the fly ash leading to artefacts especially during extraction with aromatic solvents.

The products of such reactions between toluene and fly ash were identified and the reaction mechanisms producing them investigated.

EXPERIMENTAL AND ANALYSIS

The fly ash obtained from the electrofilter system of different MWIs was first ground and extracted at room temperature for 24 hours with different solvents. All chemicals and solvents used were of great purity, suitable for trace analysis. The reactions were carried out in simple reflux apparatues with a gas inlet tube and a sampling possibility.

GC was performed on a Carlo Erba Gaschromatograph with split/splitless injector on a 5m uncoated precolumn coupled to a DB5 column (60m, 0.32mm i.d., 0.25μm filmthickness) using helium as carrier gas and FID.

The same gaschromatograph was used for GC-MS but with a splitless-on-column injector on an uncoated precolumn connected to a DB5 column (30m, 0.25mm i.d., 0.25μm filmthickness) and a Finnigan Mat mass spectrometer with Incos data system operating in electron impact mode. The observed mass range was between 70 and 300.

Identification of the substances results from the comparison of mass spectra and retention times with those from reference substances.

Quantification was carried out by determining response factors by standard solutions and naphthalene as internal standard. The reference substances synthesized were separated and purified by semipreparative HPLC using two different columns, a silica column (250-25) with n-hexane as mobile phase and a RP18 column (250-10) with methanol as mobile phase. Characterization occured by IR-, 13C-NMR- and mass spectra as well as comparing structure-chromatographic retention relationships [1,2].

RESULTS AND DISCUSSION

Remarkable products of the reaction between toluene and fly ash are the formation of $C_{14}H_{14}$ isomers. Comparing retention times and mass spectra indicates the exclusive formation of o- and p-methyldiphenylmethane (MDPM). Formation of dimethylbiphenyls (DMBP) could not be observed. A reaction mechanism for the oxidative dimerisation can be postulated by metal oxides as well as by metal chlorides.
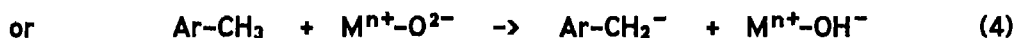
Leaching tests of the used fly ash show the same results (Tab.1) as described by investigations about mineral speciation and phases of metals on fly ash [3,4]. They have found that especially iron and copper do not exist as water-soluble chlorides. Therefore Friedel-Crafts-reactions as the Scholl reaction [5] generally leading to aryl-aryl coupling could not be observed in our experiments.

Tab.1 Leaching tests [ppm]

	Cu	Fe	Zn
aqua regia	980	22300	14000
water	<1	680	<1

Transition metal chlorides should also produce chlorinated species if the reaction takes place by a radical cation mechanism [6] which could not be observed too.

Proceeding on the assumption that to some extent the transition metals exist as oxides, supported by the leaching tests and other investigations [3,4], leads to a reaction mechanism starting with the formation of a radical cation and going further to a benzyl cation [7,8]. This cation could undergo an electrophilic substitution to another toluene molecule directing in ortho- or para-position according the mechanisms of aromatic electrophilic substitution [13]:

$$Ar-CH_3 + M^{n+} \rightarrow Ar-CH_3^{\cdot+} + M^{(n-1)+} \tag{1}$$

$$Ar-CH_3^{\cdot+} + M^{n+} \rightarrow Ar-CH_2^{+} + M^{(n-1)+} + H^{+} \tag{2}$$

$$Ar-CH_2^{+} + Ar-CH_3 \rightarrow Ar-CH_2-Ar-CH_3 + H^{+} \tag{3}$$

or $\qquad Ar-CH_3 + M^{n+}-O^{2-} \rightarrow Ar-CH_2^{-} + M^{n+}-OH^{-} \tag{4}$

$$Ar-CH_2^{-} + M^{n+} \rightarrow Ar-CH_2^{+} + M^{(n-2)+} \tag{5}$$

or $\qquad Ar-CH_2^{-} + 2M^{n+} \rightarrow Ar-CH_2^{+} + 2M^{(n-1)+} \tag{6}$

The products are o- and p-MDPM and in small quantities dibenzyl.

The methyl-methyl coupling is favoured by metals which are less basic such as the metals at the right side of the periodic table (PbO, BiO). It occurs by the intermediately formed benzyl radicals. Because of the weak basicity of the metal ion it does not abstract a hydrogen atom once more.

Quantitative results of fly ash in comparison with that of some metal oxides are shown in Tab.2. The values of the metal oxides are converted to the content of the element as found in fly ash. Enclosed the hypothetical assumption is made that the actual element would exist only in this respective modification.

Tab.2 Quantitative comparison of the MDPM-formation (yield µg/g fly ash/20h)

	fly ash	CuO	Fe_2O_3	Fe_3O_4	MnO_2	TiO_2
o-MDPM	13.3	2.1	2.0	2.9	0.25	0.6
p-MDPM	21.0	8.7	2.8	5.4	0.38	0.9
o/p-ratio	0.63	0.24	0.71	0.54	0.66	0.66

The results in Tab.2 show that the listed compounds are not the only one responsible for the formation of MDPM.

For thermodynamic considerations the basic reactions of toluene were set up and modelled in a number of ways which differ in detail.

$\Delta G°$ (T= 300-800K) has been evaluated for the various component reactions assuming that all species are gaseous. All thermodynamic data were taken from standard literature [9]. If non available, $\Delta H°_{f,298}$, $S°_{298}$ and $C_{p,298}$ were calculated using Benson's method [10].

The calculations point out that formation of MDPMs is energetically favoured compared to the formation of DMBPs. The exothermal following-reactions leading to polycondensated aromatic compounds have not been observed yet at low temperatures (<383K).

The same result has been found for the reaction of toluene and fly ash at the presence of oxygen as proton acceptor which is strong exotherm.

The formation of MDPMs and its isomer distribution has been confirmed by a variety of model mixtures with metal oxides and chlorides analogous to fly ash.

As reaction products of toluene in liquid phase benzaldehyde and benzyl alcohol have also been identified. In some cases benzoic acid has also been found in higher concentrations.

The extend of the formation of these products depends to a certain degree on concentration and reactivity of the metal oxides. The basic character and the strength of the metal-oxygen bond is of decisive importance for the formation of π-complexes [11,12] with coordinativ unsaturated cations on the surface.

CONCLUSIONS

In the temperature range of extraction processes (298-383K) oxidation reactions on fly ash dominate. Chlorination reactions have not been observed.

The oxidative coupling between two toluene molecules is the most efficient reaction utilizing surface oxygen. All other oxidation reactions require more oxygen. These reactions are caused by metal oxides of the transition elements on fly ash. The methyl-aryl coupling of toluene is produced by activ basic sites of oxygen on the surface. The basic properties of the metal oxides depend on composition of the waste, the chemistry during the incineration process and the thermal history of the fly ash.

Thermodynamic considerations show that the formation of MDPMs is energetically favoured instead of DMBPs. The more exothermic following reactions to PAHs have not been observed.

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