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Catalytic combustion of chlorobenzene on Pt/γ-Al_2O_3 in the presence of aliphatic hydrocarbons

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Abstract

During the catalytic combustion of chlorobenzene on a 2% Pt/γ-Al_2O_3 catalyst, considerable amounts of polychlorinated benzenes are formed as by-products. The co-feeding of heptane practically eliminates this unwanted side-reaction. Moreover, the conversion of chlorobenzene occurs at much lower temperatures (the $T_{50\%}$drops from 305 to 225°C). Simultaneously, the conversion of heptane is retarded. The addition of other hydrocarbons have a similar effect. Water and heat produced by the combustion of the added hydrocarbon cannot explain the increase in destruction rate of chlorobenzene. Removal of Cl from the surface by the alkane appears to be the ruling factor. ©1999 Elsevier Science B.V. All rights reserved.

1. Introduction

There is an increasing interest for catalytic processes to destroy low concentrations of chlorinated hydrocarbons in waste gases. Metal oxides, such as chromium oxides [1–3], vanadium based systems [4] and copper [5,6] are active catalysts for the combustion of chlorinated volatile organic compounds (VOCs). Formation of toxic polychlorinated by-products [5,7,8] and loss of catalytic material as volatile oxychlorides [9] are often encountered as drawbacks. An exception seems to be uranium oxide [10].

Supported noble metals, especially platinum [11–13] and palladium [14,15], can also be applied for the catalytic combustion of chlorinated VOCs. The intrinsic disadvantage of noble metals is their strong interaction with Cl. In most cases, alumina serves as the support, which also promotes the conversion of some chlorinated hydrocarbons [13,16]. In an earlier study [17], 2% Pt on γ-Al_2O_3 proved to be active in the catalytic combustion of chlorobenzene, a model compound for chlorinated aromatics. However, at temperatures at which chlorobenzene was almost completely converted, considerable amounts of polychlorinated benzenes emerged in the flue gas. The entire spectrum of congeners could be identified, ranging from di- to hexachlorobenzene. It has been shown that platinum plays an active role in this chlorination reaction. The co-feeding of steam lowered the amounts of polychlorinated benzenes.

Should one wish to destroy chlorinated aromatics in a safe and effective way, formation of polychlorinated benzenes should be avoided. In looking for a useful remedy, the co-feeding of a non-chlorinated VOC seemed attractive [13]. Furthermore, the contaminants in industrial flue gases (e.g. waste incineration) comprise chlorinated compounds and hydrocarbons (alkynes, alkenes, alkanes, and oxygenates). Only a few detailed studies on the catalytic combustion of

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mixtures can be found, although the behaviour of the mixture components is often different from that of the individual component [18]. In general, the combustion of one compound may be inhibited by the presence of another reagent due to preferential co-ordination to the catalyst [19,20].

In this paper, the results are presented concerning the influence of addition of *n*-alkanes on the performance of a 2% Pt/γ-Al_2O_3 catalyst in the combustion of chlorobenzene.

2. Experimental

The experimental procedure has been described before [17]; a short summary follows. The $H_2Pt(OH)_6$ precursor (Johnson Matthey) was applied on the γ-Al_2O_3 support (Degussa C) by homogeneous deposition precipitation. After calcination at 600°C, the BET surface of the catalyst was 95 m^2/g and Pt dispersion 16% for the 2% Pt/γ-Al_2O_3 and 18% for the 0.5% Pt/γ-Al_2O_3 catalysts.

The computer-controlled set-up [21] consisted of Brooks 5850 TR electronic mass flow controllers for the introduction of nitrogen and oxygen (both Air Products). Chlorobenzene (Baker), pentane (Acros), heptane (Baker), and decane (Acros) were introduced by flowing nitrogen through temperature-controlled impingers. In the figures, the experiments with 500 ppm chlorobenzene are compared to earlier ones with 1000 ppm. Experiments with chlorobenzene per se showed that conversion or relative amounts of by-products were independent of chlorobenzene concentration.

After heating, the gas entered the plug-flow reactor (i.d. = 12 mm), with the catalyst bed (0.3 g catalyst = 0.6 ml, particle size 125–250 μm). The GHSV at room temperature was 10 000 h^{-1}. The temperature in the catalyst bed was measured by means of a fixed insert. Normally, this temperature was slightly lower than the pre-set furnace temperature, but when large amounts of hydrocarbons are combusted, a higher temperature was measured. The values presented in this paper refer to the catalyst-bed temperatures. When an experiment was repeated with a fresh catalyst, the conversion curve was quite comparable. The approximate error in the reported $T_{50\%}$ values is ±5°C.

Products were analysed by on-line gas chromatography (HP 5890 Series II). CO and CO_2 first passed a methaniser before entering the FID detector. Non- and lower chlorinated compounds were analysed directly on FID. Higher chlorinated products have been quantified by an electron capture detector (ECD). The amounts of all compounds were calculated using methane as an external standard. Identification of products was performed using off-line GC-MSD (HP5890-5972).

3. Results

In Fig. 1, conversion curves for chlorobenzene and heptane per se, and in a 1 : 5 chlorobenzene : heptane mixture are shown. The improvement of chlorobenzene conversion is striking: $T_{50\%}$ is lowered by about 80°C. The effect on the temperature at which no chlorobenzene could be detected anymore ($T_{100\%}$) is even larger: from 440°C for chlorobenzene per se to 270°C for chlorobenzene with heptane.

Further increase of the heptane excess (8 : 1, 20 : 1), did not change $T_{50\%}$ for chlorobenzene, but complete conversion was reached at a still lower temperature. However, at higher heptane conversions a substantial temperature increase was noticed in the catalyst bed: the difference between the catalyst-bed temperature and the pre-set furnace temperature was 0°C for the 5 : 1 mixture and 25°C for the 20 : 1 mixture. This makes interpretation of the data at higher conversions ambiguous.

Conversely, the conversion of heptane is retarded by the presence of chlorobenzene: $T_{50\%}$ is increased by 50°C in the presence of chlorobenzene. The reduction of combustion efficiency of aliphatic hydrocarbons in the presence of aromatics has been observed before [20]. Note that the rate of combustion for heptane per se is much higher than that for chlorobenzene. Interestingly, heptane conversion is still rather low (~5%), while the chlorobenzene degradation amounts to >50%.

With the chlorobenzene : heptane mixtures, the output of polychlorinated benzenes is strongly suppressed. In Fig. 2, the maximum amounts (relative to the chlorobenzene input) of polychlorinated benzenes formed are shown. These maxima occur at temperatures, where conversion of chlorobenzene is almost

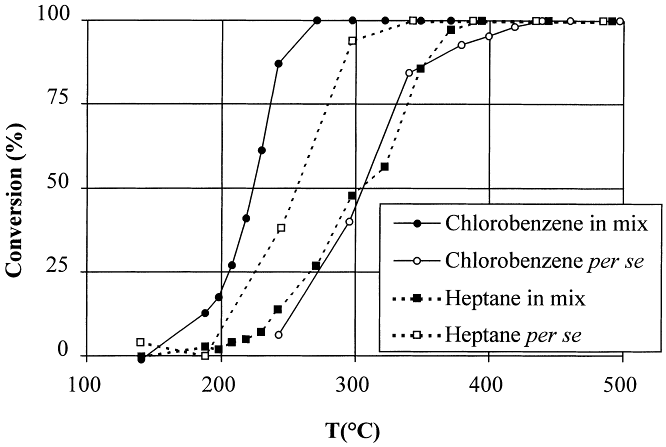

Fig. 1. Conversion of chlorobenzene (—) and heptane (··). Conditions: 15% O_2, 85% N_2, chlorobenzene per se: 1000 ppm; heptane per se: 1500 ppm; chlorobenzene + heptane: 500 ppm chlorobenzene, 1500 ppm heptane.

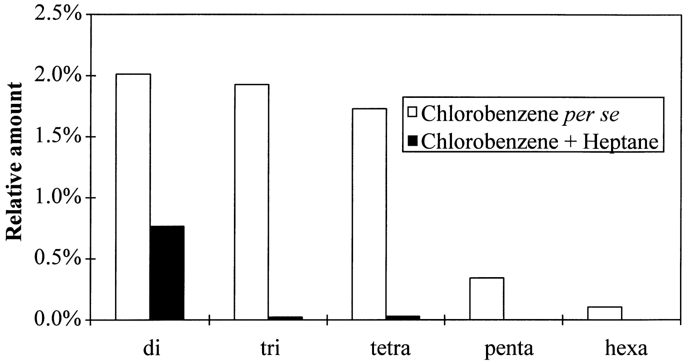

Fig. 2. Maximum levels of polychlorinated benzenes based on chlorobenzene input. Conditions: 15% O_2, 85% N_2, chlorobenzene per se: 1000 ppm chlorobenzene, $T = 420$°C; chlorobenzene + heptane: 500 ppm chlorobenzene, 1500 ppm heptane, $T = 230$°C.

complete. Only dichlorobenzene is observed with the chlorobenzene–heptane mixture, while the other congeners are below the detection limit (ca. 1 ppb). Apart from the polychlorinated benzenes, CO_2 was the only observed carbon-containing product in all experiments. Chlorinated non-aromatic hydrocarbons were not detected.

When a lower Pt loading (0.5%) was used, conversion of chlorobenzene per se was within the experimental error, the same as with the 2% Pt catalyst (see Table 1). By-product formation was, however, much lower with the 0.5% Pt/γ-Al_2O_3 (at 420°C, 1.6% based on chlorobenzene intake) than with 2% Pt system (6%). In a 1 : 5 chlorobenzene : heptane mixture, the conversion of chlorobenzene was improved. The $T_{50\%}$ decreased by 50°C to ~250°C. Polychlorinated benzenes were not detected at all.

Decane has a similar effect on chlorobenzene conversion as heptane, in fact the $T_{50\%}$ values for the mixture experiments are nearly the same (~225°C, Fig. 3). Decane conversion is retarded by about 50°C; in the mixture, the rates of conversion for decane and chlorobenzene are about equal. As with heptane, polychlorinated benzenes are formed at low levels. In Fig. 3, conversion curves for various decane concentrations are shown. Conversion of decane depends on the relative concentrations of chlorobenzene: the reaction has more difficulty to reach completion at higher relative chlorobenzene concentrations.

Table 1
$T_{50\%}$ (in °C) for chlorobenzene conversion in the absence, and presence, of hydrocarbons

Catalyst	Hydrocarbon	$T_{50\%}$[a] PhCl[b] per se	$T_{50\%}$[a] PhCl[b] in mixture	$T_{50\%}$[a] HC[c] per se	$T_{50\%}$[a] HC[c] in mix
2% Pt/γ-Al_2O_3	heptane[e]	305	225	250	300
0.5% Pt/γ-Al_2O_3	heptane[e]	305	260	n.d.[d]	325
2% Pt/γ-Al_2O_3	decane[f]	305	225	170	220
2% Pt/γ-Al_2O_3	pentane[g]	305	240	n.d.	325

[a] Error margins in $T_{50\%} = \pm 5$°C.

[b] Chlorobenzene.

[c] Hydrocarbon.

[d] Not determined.

[e] 15% O_2, 85% N_2, Chlorobenzene per se: 1000 ppm; heptane per se: 1500 ppm; chlorobenzene + heptane: 500 ppm chlorobenzene, 1500 ppm heptane.

[f] 15% O_2, 85% N_2,; Decane per se: 500 ppm; chlorobenzene + decane: 500 ppm chlorobenzene, 500 ppm decane.

[g] 15% O_2, 85% N_2; chlorobenzene + pentane: 500 ppm chlorobenzene, 1000 ppm pentane.

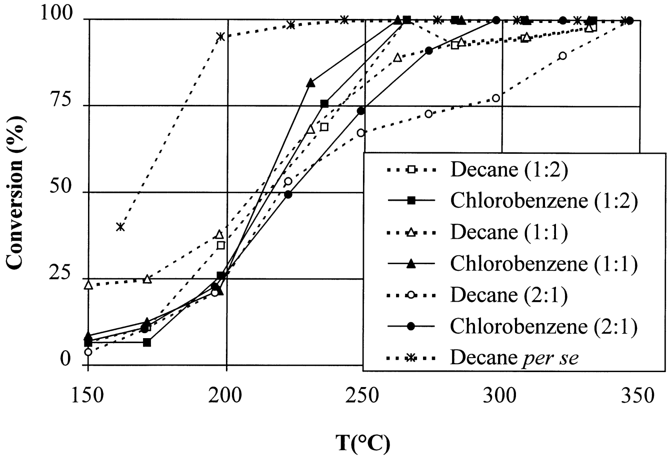

Fig. 3. Conversion of chlorobenzene (—) and decane (··). Conditions: 15% O_2, 85% N_2,; decane per se: 500 ppm; chlorobenzene + decane (2 : 1): 500 ppm chlorobenzene, 250 ppm decane; chlorobenzene + decane (1 : 1): 500 ppm chlorobenzene, 500 ppm decane; chlorobenzene + decane (1 : 2): 500 ppm chlorobenzene, 1000 ppm decane.

In a chlorobenzene–pentane mixture, the rate of chlorobenzene conversion was increased as well, albeit the increase being not as high as with heptane and decane (Table 1). In a 1 : 2 mixture, $T_{50\%}$was ~240°C, instead of 225°C for heptane and decane. The formation of polychlorinated benzenes was equally well suppressed with all alkanes.

4. Discussion

There are few examples of enhancement of rates of catalytic combustion due to co-feeding, most of which refer to chlorinated compounds. Windawi and Zhang [13] observed a decrease in $T_{50\%}$ of 200°C of trichloroethylene on Pt/Al_2O_3 in the presence of ethylene, while the addition of ethane did not change the behaviour of trichloroethylene. Sharma et al. [22] found similar effects with dichloromethane, albeit less pronounced: the conversion of dichloromethane can be accelerated by methanol or acetone using a Pt–Pd bimetallic hydrophobic catalyst.

The present results show an increased chlorobenzene combustion rate in the presence of pentane, heptane or decane, while the conversion of the hydrocarbon is retarded. The slowing down of the hydrocarbon combustion in the mixtures can be explained by competitive adsorption of chlorobenzene and the alkane. Chlorobenzene adsorbs better on the catalyst than the alkanes, because of the π-complex formation with the platinum [20,23].

Four possible reasons for an increased conversion rate for chlorinated compounds in the presence of hydrocarbons can be envisaged:

1. Additional heat production.
2. Water as a combustion product.
3. Pt remains in the more active zerovalent state.
4. Selective removal of chlorine from the surface.

4.1. Additional heat production

Barresi and Baldi [20] state that in many studies of the catalytic combustion of mixtures “the results are influenced by temperature variations in the reactor due to heat release by combustion.” Indeed, we have noticed that the catalyst-bed temperature increases due to the combustion of the aliphatic hydrocarbon, if applied in substantial proportions. However, no effect on $T_{50\%}$ for chlorobenzene is observed when the concentration of the hydrocarbon, for example decane, is increased, i.e. when more heat is produced (Fig. 3). Moreover, at $T_{50\%}$ for chlorobenzene, the heptane combustion is still at a low level (Fig. 1). Hence, although the effect of heat cannot be ruled out entirely, other factors appear to be more important.

4.2. Water as a combustion product

For chlorinated hydrocarbons, such as CH_3Cl and CH_2Cl_2, an important rate enhancement by water is observed, but this is due to hydrolysis on the γ-alumina surface [16]. In our earlier work, we have found that chlorobenzene destruction is improved and polychlorinated benzenes formation is decreased when a large excess of steam is present [17]. But the addition of hydrocarbons has a much larger impact on both, the conversion and by-product formation relative to steam. Furthermore, heptane conversion is only a few percent when $T_{50\%}$ for chlorobenzene is reached. Thus, the water production is as low as 1000 ppm, compared to a concentration of 17 500 ppm in the experiments with steam.

In this way, the water produced may to some extent improve the conversion of chlorobenzene and inhibition of by-product formation, but it is not the ruling factor.

4.3. Pt remains in the more active zero-valent state

Völter et al. [24] studied heptane combustion over Pt catalysts. They found that, with a large (6.8-fold) oxygen excess, metallic Pt is converted into Pt^{IV}-oxides, which are less active in combustion. At lower oxygen concentrations (1.4-fold excess), heptane ensures that Pt remains in the zero-valent state. We also noticed an increase in combustion efficiency and concomitant decrease in polychlorinated benzene formation when lowering the oxygen content [17]. In situ formed oxychlorides are likely to be the reactive species in the formation of polychlorinated benzenes. It has been show that Pt on alumina catalysts prepared from chloride-containing precursor, contain Pt^{IV}-oxychorides upon calcination [25,26]. Pt^{IV} oxides decompose into oxygen and zero-valent Pt above 500°C, while Pt^{IV} oxychlorides are more persistent, and are still present above 600°C [25]. However, in situ spectroscopic studies are necessary to establish the importance of Pt-oxychlorides under our conditions.

The hydrocarbons in the mixture experiments may serve as reduction agents to keep the Pt in the zero-valent state, which is more active in combustion. Also, the rate of formation of polychlorinated benzenes is expected to be extremely slow on metallic platinum. However, the oxygen concentration used in this study is quite high (6.5-fold excess), which promotes formation of Pt^{IV} species [24].

Consequently, the added hydrocarbon is not expected to be able to keep the Pt in the zero-valent form. Therefore, another mechanism must cause the active removal of Cl from the surface.

4.4. Selective removal of chlorine from the surface

Very recently, it has been shown that polychlorinated benzenes also arise in the combustion of chlorobenzene on Pd/ZeoliteY catalysts [15]. Various X-ray absorption techniques show the presence of carbon, oxygen and chlorine on the Pd surface [6]. Whether this is in the form of oxychlorides is not specified.

This is probably also the case with the Pt catalysts employed. Chlorobenzene adsorption and C–Cl bond dissociation occur at low temperatures on various metals [23,27]. At this temperature no reaction takes place, hence chlorobenzene dissociation is reversible and the Cl might block oxygen adsorption. Only at elevated temperatures, Cl is removed from the surface, e.g. as polychlorinated benzenes and HCl. Then, Pt sites are available again and chlorobenzene conversion starts.

The acceleration of chlorobenzene conversion concomitant with the suppression of polychlorination sharply suggests that the hydrocarbon causes removal of Cl from the Pt surface (at the same time reducing the Pt). How precisely this occurs is yet unknown, and further experiments — with other hydrocarbons, and/or with labelled species — are required.

Alkanes are known to react rapidly with elementary chlorine. Assuming that Pt oxychlorides are formed, Cl will be present as anions and there is no indication that the catalyst produces atomic or molecular chlorine. A possibility might be the reaction of a Pt oxychloride site with the hydrocarbon via hydrogen abstraction to create a $Pt(OH)Cl_2$ entity, which rapidly loses HCl. The second Cl can be removed by another hydrocarbon. The overall result of this process is, of course, the reduction of Pt. When the chlorine is removed from the surface, the chlorobenzene dissociative adsorption becomes irreversible and by-product formation is precluded.

5. Conclusions

The addition of pentane, heptane and decane almost eliminates the formation of polychlorinated benzenes in chlorobenzene combustion on 2% $Pt/\gamma\text{-}Al_2O_3$. Moreover, the chlorobenzene destruction is firmly accelerated.

The production of heat and the formation of water by combustion of the hydrocarbon may to some extent contribute to the acceleration of chlorobenzene conversion. The alkanes might reduce Pt to the more active zero-valent state and prevent formation of Pt^{IV}-oxychlorides, by removing Cl from the Pt-surface. Without alkanes, this Cl is removed only at higher temperatures, thus blocking the surface for chlorobenzene and oxygen adsorption.

In sum, $Pt/\gamma\text{-}Al_2O_3$ is a very active and safe catalyst in the combustion of chlorobenzene, provided that suitable hydrocarbons are present in the feed.

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