

## Catalytic oxidation of chlorobenzene, a model compound for dioxins, over Pt/zeolite catalysts

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### Introduction

Increasing emissions, especially in highly industrialized countries, of hazardous substances like persistent organic pollutants (POP) including dioxins has become a problem of vital importance. In recent years significant efforts have been made in order to reduce POP emissions (especially of chlorinated compounds) at the international level, which were translated in a series of protocols signed within the framework of several international conventions<sup>1,2</sup>. One potential answer deals with the catalytic oxidation of chlorinated organic compounds including dioxins which can operate at low temperature for the treatment of very dilute pollutants (< 1%).

Catalytic oxidation is generally carried out over three main catalyst types: TiO<sub>2</sub> based V<sub>2</sub>O<sub>5</sub>/WO<sub>3</sub> catalysts<sup>3-8</sup>, noble metals (Pt, Pd), supported on various oxides<sup>9-12</sup> and on zeolites<sup>13,14</sup>. According to recent studies the latter type of catalyst seems to be very promising towards oxidation of chlorinated compounds<sup>15</sup>. The aim of this work is to evaluate performances of a catalyst constituted of Pt deposited over a faujasite type (FAU) zeolite on the catalytic oxidation of chlorobenzene, a model molecule chosen to represent dioxins.

### Methods and Materials

All zeolite catalysts were based on a protonic faujasite (HFAU). Pt/HFAU catalysts were prepared by ion exchange with Pt<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub> (pH = 7), respectively followed by calcination under dry airflow at 500°C for 4h. All catalysts are labeled as follows: x%Pt<sub>y</sub> where x is the weight fraction of deposited platinum and y the type of support. 1%PtAl<sub>2</sub>O<sub>3</sub> catalyst, a standard oxidation catalyst prepared from a Al<sub>2</sub>O<sub>3</sub> support provided by the French Oil Institute (IFP) and 1.2%PtSiO<sub>2</sub> catalyst were obtained by impregnation and calcined at 450°C during 4 hours. The catalysts properties including the number of accessible platinum atoms (nPt) are given in Table 1.

**Table 1:** Catalysts physico-chemical properties.

Catalyst	Si/Al ratio	Pt dispersion (%)	nPt (x 10 <sup>18</sup> atoms.g <sup>-1</sup> )
1%PtAl <sub>2</sub> O <sub>3</sub>	-	78 <sup>a</sup>	23.85
1.2%PtSiO <sub>2</sub>	-	50 <sup>c</sup>	18.53
HFAU	5	0	0
0.1%PtHFAU	5	40 <sup>a</sup>	1.66
0.2%PtHFAU	5	16 <sup>a</sup>	1
0.3%PtHFAU	5	10 <sup>a</sup>	0.97
0.6%PtHFAU	5	8 <sup>a</sup>	1.45
0.8%PtHFAU	5	25 <sup>d</sup> (18 <sup>b</sup> )	6.17
1.1%PtHFAU	5	52 <sup>a</sup>	17.5

<sup>a</sup> estimated from toluene hydrogenation<sup>16</sup>

<sup>b</sup> estimated from CO adsorption followed by infra-red spectroscopy

<sup>c</sup> estimated from hydrogen chemisorption

<sup>d</sup> estimated from transmission electronic microscopy (TEM).

Catalytic activity tests were carried out in a fixed-bed reactor (i.d = 10 mm), at atmospheric pressure in the 250-350°C range using 0.14 g of catalyst (grain size between 200 and 400µm). Before reaction catalyst samples were pretreated in situ under dry air flow (90 ml.min<sup>-1</sup>) at 350°C for 6h, then cooled down to the reaction temperature. C<sub>6</sub>H<sub>5</sub>Cl was introduced into the reactor using a bubbling flask containing C<sub>6</sub>H<sub>5</sub>Cl swept by a dry air flow, leading to a gaseous mixture directed to a condenser maintained at -16°C. The resulting effluent was then mixed with wet air to ensure that hygrometric level was matching industrial conditions. The reactant mixture contained then 1.03% of H<sub>2</sub>O (corresponding to an hygrometry of about 50%) and 667 ppm of C<sub>6</sub>H<sub>5</sub>Cl. The total gas flow was 75 ml min<sup>-1</sup> with a GHSV of 18000 h<sup>-1</sup>. The expected reaction is the complete oxidation of chlorobenzene into CO<sub>2</sub>, H<sub>2</sub>O and HCl:

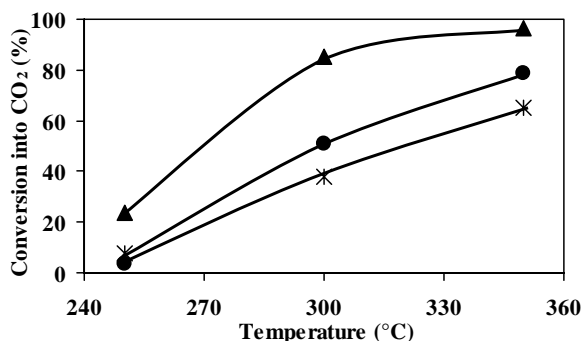


The reaction products were analyzed using an on-line gas chromatograph, equipped with FID detector and VF- 5ms column for the analysis of C<sub>6</sub>H<sub>5</sub>Cl and PhCl<sub>x</sub> and with a TCD detector and Porapak Q column for CO<sub>2</sub> analysis. The carbon balance, including the amount of carbon deposited on the catalyst, was always higher than 98%.

## Results and Discussion

**Oxidation of chlorobenzene over Pt catalysts. Influence of the support:** Figure 1 shows that at similar platinum content 1.1%PtHFAU is the best catalyst for chlorobenzene oxidation, activities order being the following: PtHFAU > PtAl<sub>2</sub>O<sub>3</sub> > PtSiO<sub>2</sub>. At 350°C, chlorobenzene was totally destructured over PtHFAU with selectivity into CO<sub>2</sub> close to 97.5%, the chlorobenzene conversion being equal to 81% and 74% respectively over Pt/Al<sub>2</sub>O<sub>3</sub> and PtSiO<sub>2</sub>.

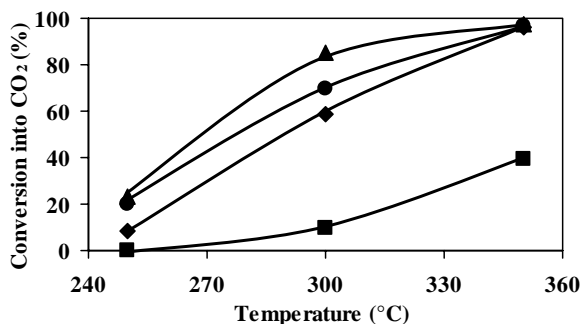
**Figure 1:** Conversion of chlorobenzene into CO<sub>2</sub> taken after 4h reaction as a function of the reaction temperature over 1%PtAl<sub>2</sub>O<sub>3</sub> (●), 1.2%PtSiO<sub>2</sub> (✱) and 1.1%PtHFAU(▲) catalysts.



It is well known that the more often observed by-products in chlorobenzene oxidation are polychlorobenzenes (PhCl<sub>x</sub>)<sup>9-11,14</sup>. At 50°C dichlorobenzenes were the main by-products. However, PtHFAU catalyst is the more selective: PhCl<sub>x</sub> represent only 3.5 ppm in effluent gas versus 14 ppm and 25 ppm respectively for PtSiO<sub>2</sub> and PtAl<sub>2</sub>O<sub>3</sub>. No deactivation was observed during 4 day's reaction over 1.1PtHFAU catalyst at 300°C. Furthermore, selectivity into PhCl<sub>x</sub> decreases with time on stream.

**Influence of platinum content over PtHFAU catalysts:** The influence of the platinum content and/or of the number of accessible platinum atoms per gram of catalyst (nPt) was specified for chlorobenzene oxidation at various temperatures by using a series of PtHFAU catalysts (Si/Al = 5) with platinum contents varying from 0 to 1.1 wt% hence differing largely by nPt: from 0 to 17.5x10<sup>18</sup> atoms.g<sup>-1</sup> (Table 1). The conversion of chlorobenzene into CO<sub>2</sub> reported after 4h reaction, increases with the reaction temperature and the platinum content (Figure 2).

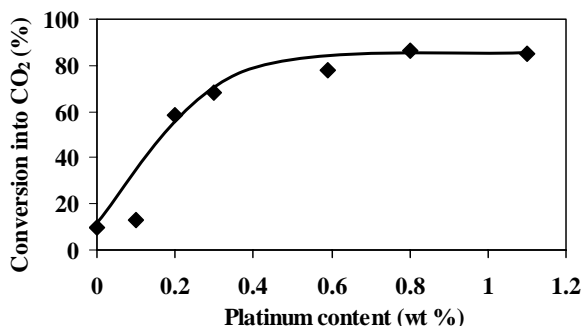
**Figure 2:** Conversion of chlorobenzene into CO<sub>2</sub> after 4h reaction as a function of the reaction temperature over 0(■), 0.2(◆), 0.3(●), and 1.1%(▲) PtHFAU catalysts.



Whatever the platinum content, PtHFAU catalysts are able to oxidize totally chlorobenzene at 350°C. Furthermore at this temperature, 40 % of chlorobenzene can be oxidized into CO<sub>2</sub> over the

zeolitic support. The evolution of chlorobenzene oxidation was reported after 4h reaction at  $T = 300^{\circ}\text{C}$  as a function of platinum content (Figure 3).

**Figure 3:** Conversion of chlorobenzene into  $\text{CO}_2$  after 4 h reaction at  $300^{\circ}\text{C}$  as a function of the content of platinum over PtHFAU catalysts.



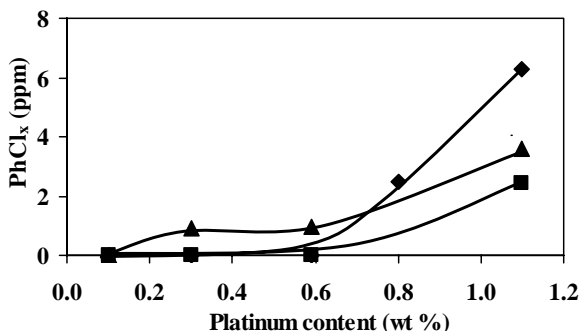
Conversion into  $\text{CO}_2$  increases with the platinum content (whatever the Pt dispersion) and for  $\text{Pt} \geq 0.6\text{wt}\%$  a quasi plateau was observed. This behavior is characteristic of a bifunctional mechanism: at high Pt content, activity of the support is the limiting step compared to oxidative activity of the metal. This tends to show that chlorobenzene is pre-transformed over zeolitic support before its final oxidation over platinum particles. Moreover,  $\text{CO}_2$  selectivity was greater than 90% from 0.2%PtHFAU and from 0.1 to 0.6wt% Pt, only benzene with a concentration below 1 ppm was detected as by-product (Table 2).

**Table 2:** Conversion into polychlorinated compounds and selectivity into  $\text{CO}_2$  (after 4h reaction) during oxidation at  $300^{\circ}\text{C}$  with 667 ppm chlorobenzene over PtHFAU catalysts

Catalysts	nPt acc ( $\times 10^{18}$ at.g $^{-1}$ )	$\text{C}_6\text{H}_5\text{Cl}$ conv. (%)	Select. into $\text{CO}_2$ (%)	$\text{PhCl}_x$		$\text{C}_6\text{H}_6$		%C
				ppm	%	ppm	%	
HY5	0	11.5	85.8	-	-	-	-	0.19
0.1%PtHY5	1.66	17.0	76	-	-	0.17	0.15	0.23
0.2%PtHY5	-	65.7	89	-	-	0.43	0.07	n.d.
0.3%PtHY5	0.97	69.5	94.8	-	-	1	0.15	0.71
0.6%PtHY5	1.45	82.7	94.5	-	-	0.93	0.11	0.6
0.8%PtHY5	6.17	90.7	95.4	2.47	0.35	1.03	0.17	0.75
1.1%PtHY5	17.5	87.3	97.7	6.28	1.08	0.58	0.1	0.39

At  $300^{\circ}\text{C}$   $\text{PhCl}_x$  and benzene were the main detected by-products, coke was also formed on the catalysts.  $\text{PhCl}_x$  by-products appear only from 0.8%PtHFAU, the main by-products being 1,3-dichlorobenzene and 1,4-dichlorobenzene. Trichlorobenzenes were never detected at this temperature. The evolution of  $\text{PhCl}_x$  (in ppm, produced after 4 h reaction) was reported for each temperature as a function of platinum level (Figure 4).

**Figure 4:** Production of dichlorobenzene ( $\text{PhCl}_x$ ) after 4h reaction as a function of the platinum content over PtHFAU catalysts at 250°C(■), 300°C(◆) and 350°C(▲).



As it was reported for PtBEA catalysts<sup>14</sup>,  $\text{PhCl}_x$  formation presents a maximum at 300°C on 1.1%PtHFAU. Furthermore, it is clear that  $\text{PhCl}_x$  production increases with the platinum content. At 250 and 300°C  $\text{PhCl}_x$  were found from 0.6 wt% Pt. It was previously suggested that the chlorination reaction takes place the platinum particles<sup>9,12,13</sup>, and that platinum oxychlorides would be the active species in the formation of polychlorinated benzenes over  $\text{PtAl}_2\text{O}_3$  catalysts.

In this condition, the presence of reduced Pt species ( $\text{Pt}^0$ ) would be favorable to limit  $\text{PhCl}_x$  formation. Moreover it was shown that  $\text{Pt}^0$  species deposited on zeolites are the more active species for aromatic hydrocarbons oxidation<sup>17</sup>.

In this way, 0.8%PtHFAU was pre-reduced at 450°C under hydrogen, before chlorobenzene oxidation at 300°C. Unfortunately, the particular effect of this pre-reduction treatment was to increase  $\text{PhCl}_x$  formation from 2.47 to 24.84 ppm (Table 3).

**Table 3:** Selectivity into  $\text{CO}_2$  and conversion into  $\text{PhCl}_x$  compounds after 4h reaction at 300°C during oxidation with 667 ppm chlorobenzene over pre-reduced and non-reduced PtHFAU catalysts.

Catalysts	$\text{C}_6\text{H}_5\text{Cl}$ conv.(%)	Selectivity into $\text{CO}_2$ (%)	$\text{PhCl}_x$		$\text{C}_6\text{H}_6$		%C
			ppm	(%)	ppm	(%)	
0.8%PtHFAU	90.7	95.36	2.47	0.37	0.58	0.17	0.75
0.8%PtHFAU <sup>a</sup>	96.43	89.5	24.84	3.86	-	-	n.d.

<sup>a</sup> pre-reduced catalysts (at 450°C under hydrogen)

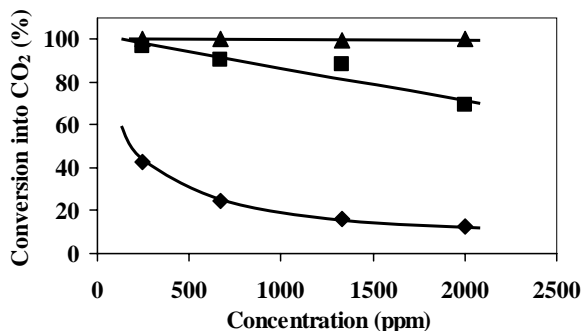
n.d. not determined

The initial presence of reduced  $\text{Pt}^0$  species in this catalyst would be then responsible for a large part to the formation of  $\text{PhCl}_x$  during chlorobenzene oxidation. Most probably, reduced Pt particles are more easily chlorinated leading to Pt chlorides or oxychlorides (since Pt is in oxidative environment) able to catalyze polychlorobenzene formation.

**Influence of the chlorobenzene concentration:** The effect of the chlorobenzene concentration (from 246 to 2000 ppm) was established over 0.8%PtHFAU catalyst between 250 and 350°C. The

chlorobenzene oxidation was always close to 100% at 350°C and decreases with increasing chlorobenzene concentration for 250 and 300°C (figure 5). At 250°C (low conversion) the reaction order in oxidation with respect to chlorobenzene was estimated to 0.3. At low concentration (e.g. 667 ppm), maximum PhCl<sub>x</sub> yields was found at 300°C. On the other hand PhCl<sub>x</sub> yield increases with increasing temperature at higher concentration, about 20 ppm of PhCl<sub>x</sub> was formed at 350°C for 2000 ppm of chlorobenzene in the feed.

**Figure 5:** Conversion into CO<sub>2</sub> after 4h reaction as a function of initial concentration in C<sub>6</sub>H<sub>5</sub>Cl over 0,8%PtHFAU catalysts at 250°C(◆), 300°C(■) and 350°C(▲).



These results obtained over Pt/zeolite catalysts are very interesting for the oxidative destruction of very diluted chlorinated compounds such as dioxins. On the other hand, our results show that only a low amount of platinum is necessary to oxidize chlorobenzene without any production of polychlorinated by-products. Furthermore, it is possible to expect excellent conversion and selectivity into CO<sub>2</sub> at low temperature (e.g. 250°C) for the oxidative destruction of chlorinated pollutants present as traces.

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## REMEDIATION METHODS AND CONTROL TECHNIQUES

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