

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

Mihaela Taralunga¹, Jérôme Mijoin¹, Patrick Magnoux¹

¹Laboratoire de Catalyse en Chimie Organique, Poitiers

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^{1,2}. 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: TiO₂ based V₂O₅/WO₃ catalysts³⁻⁸, noble metals (Pt, Pd), supported on various oxides⁹⁻¹² and on zeolites^{13,14}. According to recent studies the latter type of catalyst seems to be very promising towards oxidation of chlorinated compounds¹⁵. 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 Pt₂(NH₃)₄Cl₂ (pH = 7), respectively followed by calcination under dry airflow at 500°C for 4h. All catalysts are labeled as follows: x%Pt_y where x is the weight fraction of deposited platinum and y the type of support. 1%PtAl₂O₃ catalyst, a standard oxidation catalyst prepared from a Al₂O₃ support provided by the French Oil Institute (IFP) and 1.2%PtSiO₂ 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 ¹⁸ atoms.g ⁻¹)
1%PtAl ₂ O ₃	-	78 ^a	23.85
1.2%PtSiO ₂	-	50 ^c	18.53
HFAU	5	0	0
0.1%PtHFAU	5	40 ^a	1.66
0.2%PtHFAU	5	16 ^a	1
0.3%PtHFAU	5	10 ^a	0.97
0.6%PtHFAU	5	8 ^a	1.45
0.8%PtHFAU	5	25 ^d (18 ^b)	6.17
1.1%PtHFAU	5	52 ^a	17.5

^a estimated from toluene hydrogenation¹⁶

^b estimated from CO adsorption followed by infra-red spectroscopy

^c estimated from hydrogen chemisorption

^d 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⁻¹) at 350°C for 6h, then cooled down to the reaction temperature. C₆H₅Cl was introduced into the reactor using a bubbling flask containing C₆H₅Cl 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 H₂O (corresponding to an hygrometry of about 50%) and 667 ppm of C₆H₅Cl. The total gas flow was 75 ml min⁻¹ with a GHSV of 18000 h⁻¹. The expected reaction is the complete oxidation of chlorobenzene into CO₂, H₂O and HCl:

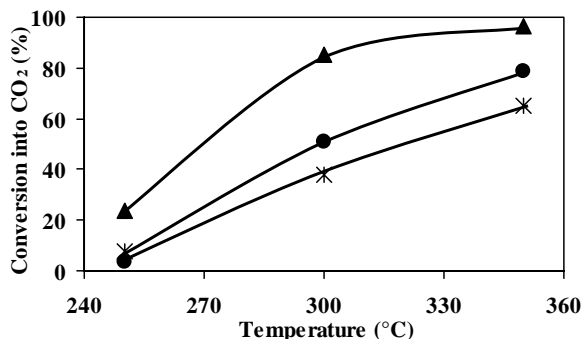


The reaction products were analyzed using an on-line gas chromatograph, equipped with FID detector and VF- 5ms column for the analysis of C₆H₅Cl and PhCl_x and with a TCD detector and Porapak Q column for CO₂ analysis. The carbon balance, including the amount of carbon deposited on the catalyst, was 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 > PtAl₂O₃ > PtSiO₂. At 350°C, chlorobenzene was totally destructured over PtHFAU with selectivity into CO₂ close to 97.5%, the chlorobenzene conversion being equal to 81% and 74% respectively over Pt/Al₂O₃ and PtSiO₂.

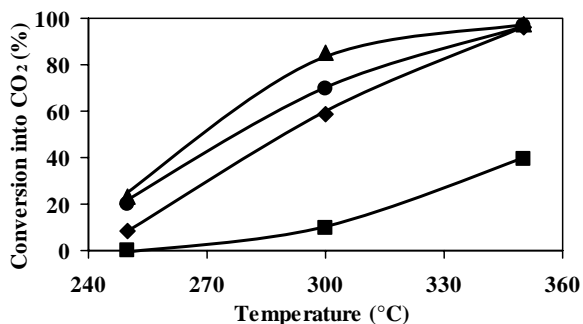
Figure 1: Conversion of chlorobenzene into CO₂ taken after 4h reaction as a function of the reaction temperature over 1%PtAl₂O₃(●), 1.2%PtSiO₂(*) and 1.1%PtHFAU(▲) catalysts.



It is well known that the more often observed by-products in chlorobenzene oxidation are polychlorobenzenes (PhCl_x)^{9-11,14}. At 50°C dichlorobenzenes were the main by-products. However, PtHFAU catalyst is the more selective: PhCl_x represent only 3.5 ppm in effluent gas versus 14 ppm and 25 ppm respectively for PtSiO₂ and PtAl₂O₃. No deactivation was observed during 4 day's reaction over 1.1PtHFAU catalyst at 300°C. Furthermore, selectivity into PhCl_x 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 17.5x10¹⁸ atoms.g⁻¹ (Table 1). The conversion of chlorobenzene into CO₂ reported after 4h reaction, increases with the reaction temperature and the platinum content (Figure 2).

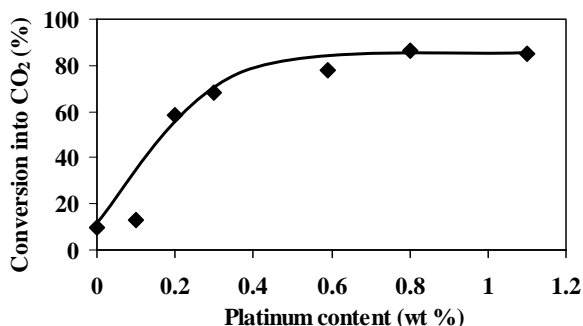
Figure 2: Conversion of chlorobenzene into CO₂ after 4h reaction as a function of the reaction temperature over 0(■), 0.2(◆), 0.3(●), and 1.1%(▲) PtHFAU catalysts.



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 CO₂ over the

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

Figure 3: Conversion of chlorobenzene into CO_2 after 4 h reaction at 300°C as a function of the content of platinum over PtHFAU catalysts.



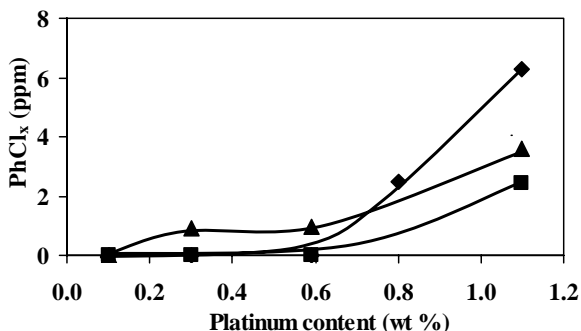
Conversion into CO_2 increases with the platinum content (whatever the Pt dispersion) and for $\text{Pt} \geq 0.6\text{wt}\%$ a quasi plateau was observed. This behavior is characteristic of a bifunctional mechanism: at high Pt content, activity of the support is the limiting step compared to oxidative activity of the metal. This tends to show that chlorobenzene is pre-transformed over zeolitic support before its final oxidation over platinum particles. Moreover, 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 CO_2 (after 4 h reaction) during oxidation at 300°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 CO_2 (%)	PhCl_x		C_6H_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°C PhCl_x and benzene were the main detected by-products, coke was also formed on the catalysts. 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 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 (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 catalysts¹⁴, PhCl_x formation presents a maximum at 300°C on 1.1%PtHFAU. Furthermore, it is clear that PhCl_x production increases with the platinum content. At 250 and 300°C PhCl_x were found from 0.6 wt% Pt. It was previously suggested that the chlorination reaction takes place the platinum particles^{9,12,13}, and that platinum oxychlorides would be the active species in the formation of polychlorinated benzenes over PtAl_2O_3 catalysts.

In this condition, the presence of reduced Pt species (Pt^0) would be favorable to limit PhCl_x formation. Moreover it was shown that Pt^0 species deposited on zeolites are the more active species for aromatic hydrocarbons oxidation¹⁷.

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 PhCl_x formation from 2.47 to 24.84 ppm (Table 3).

Table 3: Selectivity into CO_2 and conversion into 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 CO_2 (%)	PhCl_x		C_6H_6		%C
			ppm	(%)	ppm	(%)	
0.8%PtHFAU	90.7	95.36	2.47	0.37	0.58	0.17	0.75
0.8%PtHFAU ^a	96.43	89.5	24.84	3.86	-	-	n.d.

^a pre-reduced catalysts (at 450°C under hydrogen)

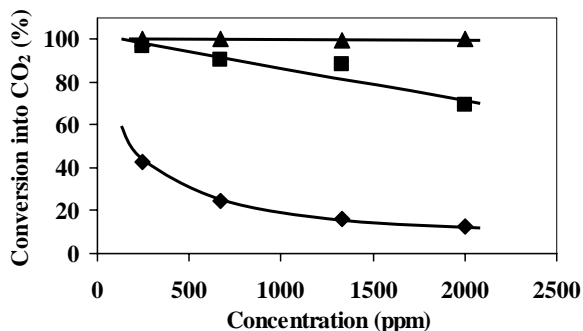
n.d. not determined

The initial presence of reduced Pt^0 species in this catalyst would be then responsible for a large part to the formation of 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_x yields was found at 300°C. On the other hand PhCl_x yield increases with increasing temperature at higher concentration, about 20 ppm of PhCl_x was formed at 350°C for 2000 ppm of chlorobenzene in the feed.

Figure 5: Conversion into CO_2 after 4h reaction as a function of initial concentration in $\text{C}_6\text{H}_5\text{Cl}$ 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_2 at low temperature (e.g. 250°C) for the oxidative destruction of chlorinated pollutants present as traces.

Acknowledgements

M. Taralunga gratefully acknowledges the Agence de l'Environnement et de la Maîtrise de l'Energie (ADEME) and the Région Poitou-Charentes for a scholarship.

References

- [1] Convention on Long-range Transboundary Air Pollution, Aarhus (Denmark), 24 June 1998.
- [2] Convention on Persistent Organic Pollutants, Stockholm (Sweden), 22 May 2001.
- [3] H. Fahlenkamp, G. Mittelbach, H. Hagenmaier, H. Brunner and K.H. Tichaczek, VGB Kraftwerkstechnik (1991) 7, 71.
- [4] H. Hagenmaier, K.H. Tichaczek, H. Brunner, G. Mittelbach, Organohalogen Compounds (1990) 3, 65.
- [5] S. Krishnamoorthy, JP Baker, MD Amaridis, Catalysis Today (1998) 40, 39.
- [6] R. Weber, S. Sakurai, H. Hagenmaier. Applied Catalysis B: Environmental (1999) 20, 249.
- [7] Y. Ide, K. Kashiwabara, S. Okada, T. Mori and M. Hara, Chemosphere (1996) 32, 189.
- [8] M. Stoll, J. Furrer, H. Seifert, G. Schaub, D. Unruh, Waste Management (2001) 21, 457.
- [9] R. W. van den Brink, M. Krzan, M. M. R. Feijen-Jeurissen, R. L. Louw, P. Mulder, Appl. Catal. B: Environ. (2000) 24, 255.

- [10] R.W. van den Brink, R. Louw, P. Mulder, Appl. Catal. B:Environ. (1998) 16, 219.
- [11] R. W. van den Brink, P. Mulder and R. Louw, Catal.Today (1999) 54, 101.
- [12] S. Krishnamoorthy, J.P. Baker, M.D. Amiridis, Catal. Today (1998) 40, 39
- [13] L. Becker, H. Förster, J. Catal. (1997) 170, 200
- [14] S. Sciré, S. Minico. C. Cristafulli, Appl. Catal. B : Environ. (2003) 45, 117.
- [15] L. Pinard, J. Mijoin, P. Magnoux and M. Guisnet, J. Catal. (2003) 215, 234.
- [16] J. Chupin, N.S. Gnep, S. Lacombe, M. Guisnet, Appl. Catal. A. (2001) 206, 43
- [17] J. Tsou, L. Pinard, P. Magnoux, J.L. Figueiredo, M. Guisnet, Appl. Catal. B. (2003) 46, 371.