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NOTE

Oxidative Decomposition of Chlorobenzene Catalyzed by Palladium-Containing Zeolite Y

Increasing emission of hazardous substances, especially in highly industrialized countries, has become a problem of vital importance. In recent years significant efforts have been made to develop adequate methods for the reduction of harmful gaseous emissions. In the case of volatile organic compounds, catalytic deep oxidation is a very efficient technique for waste gas cleaning. Several review articles available in the literature (1–11) describe the application of catalytic oxidation as a method for emission control. Compared with conventional oxidation or combustion the advantages of this method are: (i) widespread application, (ii) low energy costs, (iii) decreased NO_x formation, and (iv) small and mobile plants.

Zeolites have unique properties as catalysts. Transition metal cations or acid sites introduced into the well-defined zeolite framework by ion exchange have a decisive impact on their catalytic activity. A recently published review article deals with the application of zeolites in environmental catalysis (12). The present work deals with the oxidative decomposition of chlorobenzene catalyzed by PdY. Mochida *et al.* showed that PdY is an active catalyst for deep oxidation of hydrocarbons such as ethylene, propylene (13), and cyclohexane (14, 15), which could be confirmed also for the combustion of benzene and some of its methyl derivatives (16). This encouraged us to extend these investigations to chlorinated compounds.

Chlorobenzene (CBz), as the simplest of the chloroarenes, was chosen as a suitable model compound for the study of the zeolite-catalyzed deep oxidation of chlorinated aromatics, a group of organic compounds pertinent to the environmental debate. Well-known examples are the highly toxic polychlorinated dioxins (PCDDs) and dibenzofuranes (PCDFs) formed in municipal incinerators. In this context chlorobenzene is known to be an important precursor for PCDDs and PCDFs (17–19).

There are already some papers concerned with the catalytic combustion of chlorinated aliphatics over zeolites (20–23). However, little is yet known about the oxidative decomposition of chloroarenes using zeolitic materials as catalysts. Generally, only limited information concerning the catalytic deep oxidation of CBz is available in the literature. Laidig *et al.* (24) used an Al_2O_3 carrier containing 10 wt.% $CuO-Cr_2O_3$ as an oxidation catalyst at 823 K. Other authors have described the oxidative decomposition of CBz in a gaseous mixture together with other organic components. The use of Pt/Al_2O_3 as a catalyst for the combustion of a mixture of benzene, toluene, cyclohexane, and chlorobenzene at 573–723 K has been reported (25). A catalyst denoted as 0.15% Pt−O was used to convert a xylene/chlorobenzene mixture at 723 K (26). A major problem when chlorinated substances are converted over catalysts is poisoning of the catalyst surface (27). Thus, active sites may be blocked by chlorine, the crystalline structure of the carrier may collapse by reaction with the evolved HCl, or metal–chlorine species may be vaporized. Furthermore, there have also been investigations about the photocatalytic (28, 29), thermal (30), and biological (31) destruction of chlorobenzene.

In a previous publication (32), we reported on the application of EXAFS, XANES, and dispersive EXAFS to investigate details of the oxidative conversion of CBz over PdY. In the present paper we focus on PdY and protonated PdY (PdHY) as catalysts. Besides obtaining more information about mechanistic processes, our interest has centered on the optimization of crucial parameters such as metal content, catalyst temperature, contact time, and composition of the feed.

NH_4Y (as the precursor for PdHY) and PdY zeolites were obtained by conventional ion exchange using powdered NaY (Akzo) and aqueous solutions containing known concentrations of NH_4NO_3 (Merck) and $[Pd(NH_3)_4](NO_3)_2$ (Aldrich). For the synthesis of PdHY, previously prepared NH_4Y (see Table 1) was used. The unit cell composition of the NaY applied was determined by means of AAS (Na) and gravimetric (SiO_2) and volumetric (Al) analysis and may be represented as $Na_{54}(AlO_2)_{54}(SiO_2)_{135} \cdot 240\ H_2O$.

The exchange procedure was carried out by stirring the unbuffered suspensions for 24 h at room temperature. Subsequently, the zeolite samples were first separated by centrifugation, then washed with bidistilled water until wash solutions were nitrate free, and finally dried at 383 K in an oven. For each exchange run wash solutions were combined and analyzed for Pd and Na ions using ICP/AES. Thus the

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TABLE 1

Chemical Composition of the Zeolite Samples after Activation in Oxygen [$Y = (AlO_2)_{54}(SiO_2)_{135}$]

Sample	Composition	Exchange level (%)	Metal content (wt.%)
PdY-2.0	$Pd_{2.5}Na_{49}Y$	9.3	2.0
PdY-7.6	$Pd_{9.5}Na_{35}Y$	35	7.6
PdY-14.6	$Pd_{19}Na_{16}Y$	70	14.6
NH_4Y	$(NH_4)_{33}Na_{21}Y$	61	—
PdHY-2.0	$H_{32}Pd_{2.3}Na_{17.4}Y$	59(H), 8.5(Pd)	2.0

number of ions introduced into the zeolite matrix could be determined. For details of sample designation and composition, see Table 1.

The zeolite samples were pressed to tablets, crushed, and sieved to give grains with particle sizes between 0.3 and 0.5 mm. Before reaction the samples were activated by heating them to 723 K in an oxygen flow of ca. 20 ml/min in the flow apparatus used for the activity tests (see below). To ensure a defined state of hydration, the zeolites were stored over a saturated $CaCl_2$ solution.

The reactions were carried out in a flow apparatus consisting of a gas line with pressure control, a reservoir for CBz, a fixed bed reactor made of Pyrex glass (9 cm height, 1.4 cm diameter), and two injection valves with sample loops ($V = 5.2$ ml). Usually standard runs of 6 h time on stream (TOS) were carried out. For on-line analyses the gaseous samples were injected into gas chromatographs (GC). One was equipped with two packed columns in series. The first (1/8″ × 2 m) was filled with Porapak N (Chrompack) and the second (1/4″ × 2 m) with CTR I (Altech). This GC used for CO/CO_2 analyses was equipped with a thermal conductivity detector (GC/TCD). For the feed control and the analysis of the organic components in the effluent gas stream, a GC provided with a packed column (1/8″ = 2 m) filled with SE30 on Chromosorb (Chrompack) and a flame ionization detector (GC/FID) was used. Analytical grade reagents (Merck) and gases (Linde) were used as carrier gases as well as calibration materials. The chromatograms were evaluated using suitable computer programs. Chlorine and HCl were detected by an analytical tube for chlorine detection from Draeger, Lübeck (detection limit 0.2 ppm) and by volumetric analysis, respectively. Detection and quantification of the organic by-products were made by high-resolution GC/MS as follows: column 50 m CP-Sil8CB (Chrompack), linear velocity 35 cm/s, sample volume 1 μl, injection temperature 523 K; temperature program: initial temperature 333 K (3 min), heating rate 6 K/min, final temperature 573 K.

After a defined volume of catalyst had been activated *in situ*, the gas line was switched to the appropriate gas. The flow rate was controlled by a needle valve. The catalyst was heated to the desired temperature, which was always measured at the upper edge of the catalyst bed. Each run was started by directing the gas stream through the CBz reservoir onto the catalyst. The contact time (τ) was obtained by dividing the catalyst volume (V_{cat}) by the flow rate (F).

As already reported (32), CuY containing 4.8 wt.% Cu showed a high initial activity ($T_{cat} = 523$–623 K; $\tau = 1$–6 s; $c_{CBz} = 23$, 37 mg/liter). However, after a certain time on stream, deactivation of the catalyst occurred and deposition of crystalline by-products, identified as congeners of polychlorinated benzenes (PCBzs), could be observed at the exhaust of the reactor. These PCBzs were the only organic by-products released from the surface. Oxygenated compounds such as phenols, PCDDs, and PCDFs were not detected in any of the runs (detection limit of HRGC/MS ca. 1 ng).

Figure 1 shows that not only does the activity of PdY rise with increasing Pd content but also the yield of HCl and, to a certain extent, the yield of PCBzs. The following solid PCBzs were detected: trichlorobenzene, tetrachlorobenzene, pentachlorobenzene, and hexachlorobenzene. As Fig. 1 reveals, the chlorine balance, calculated as HCl plus PCBzs, only reaches a value of about 40 mol%. This suggests a strong interaction between Cl (present as Cl^- or organically bound chlorine) and the zeolite.

PdY-2.0 and PdY-14.6 were used to study the influence of the temperature on the activity and the product distribution. As the data listed in Table 2 show, a drastic increase of activity occurs when the reaction temperature is raised. This is, however, accompanied by an increased yield of PCBzs.

Improved results concerning the product distribution could be achieved when protonated samples were used as catalysts at high temperature (see Table 3). Under the conditions given, there is a further increase of HCl yield when protons are introduced into the zeolite lattice. Moreover, increasing oxygen concentration in the feed from 20 to 40 vol.% suppressed the formation of PCBzs.

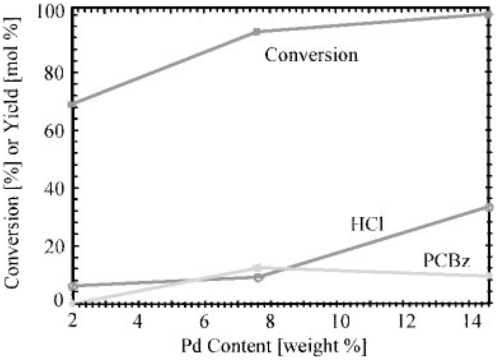

FIG. 1. Activity and yield of HCl and PCBzs for CBz oxidation over samples with various Pd contents. $T_{cat} = 573$ K; $m_{cat} = 2.2$–2.4 g; $V_{cat} = 3$ ml; $F = 120$ ml/min; $\tau = 1.5$ s; $c_{CBz} = 23$ mg/liter; TOS = 6 h.

TABLE 2

Influence of the Catalyst Temperature on Conversion and Product Yield for PdY-2.0 and PdY-14.6

Sample:	PdY-2.0	PdY-2.0	PdY-14.6	PdY-14.6
Temperature (K)	573	623	523	573
Conversion (%)	69	99.9	51	100
Products (mol%)				
HCl	6	10	30	33
C_6H_6	<0.01	n.d.	<0.01	n.d.
$C_6H_4Cl_2$	<0.01	n.d.	<0.01	n.d.
$C_6H_3Cl_3$	n.d.	n.d.	n.d.	0.5
$C_6H_2Cl_4$	n.d.	n.d.	n.d.	4
C_6HCl_5	n.d.	2	n.d.	4
C_6Cl_6	n.d.	25	0.01	1

Note. Limit of quantification ca. 0.01 mol% (n.d., not detected). $V_{cat} = 3$ ml; $\tau = 1.5$ s; $c_{CBz} = 23$ mg/liter; $c(O_2) = 20$ vol.%; TOS = 6 h; $F = 120$ ml/min; $m_{cat} = 2.2$–2.4 g.

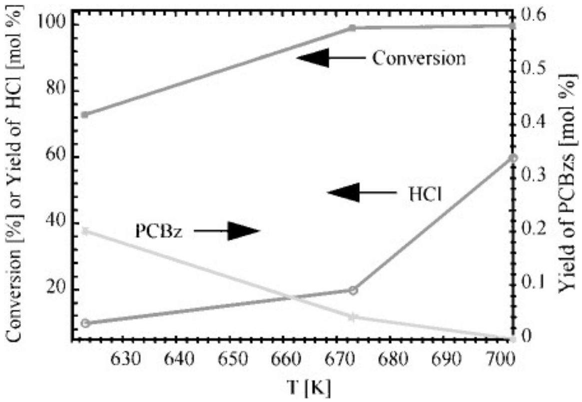

FIG. 2. Influence of the temperature at high O_2 concentration (40 vol.%) on the catalytic properties of PdHY-2.0. $V_{cat} = 1$ ml; $\tau = 1$ s; $c_{CBz} = 37$ mg/liter; TOS = 6 h; $m_{cat} = 0.7$ g; $F = 60$ ml/min.

Considering these results, we maintained the O_2 concentration at 40 vol.% in later runs. The excellent catalytic properties of PdHY-2.0 for CBz oxidation prompted us to reduce the contact time from 1.5 to 1 s at reaction temperatures between 623 and 703 K. The consequences of higher temperatures on the formation of HCl and PCBzs are shown in Fig. 2. No PCBzs were detected at 703 K. Simultaneously, the HCl yield reached 60 mol%. In order to test the long-term behavior of PdHY-2.0, we extended the experiments to allow a longer time on stream. After about 18 h, however, traces (ca. 10 μg) of pentachlorobenzene could be detected.

Bearing in mind that protons linked to the zeolite matrix have a favorable influence on the reaction pathway, we tried to find out whether introducing additional hydrogen with the feed would have a similar effect. Thus, we used a mixture of CBz and *m*-xylene. Again, deposition of solid by-products could be observed. In this case the crystalline solids turned out to be Cl-substituted *m*-xylene derivatives.

PdY has been shown to be active as a catalyst for the deep oxidation of chlorobenzene. Initially present Pd(II) is almost completely reduced within a few minutes after contact with CBz, while PdHY samples remain in an oxidized Pd state (32). On Pd(0) phases a complex mixture of chlorine, oxygen, carbon, and hydrogen is present (33). Deactivation occurs at low temperatures (623 K and lower). At high temperature (703 K) constant conversion levels as high as 100% can be achieved, although this is accompanied by transchlorination. As no deactivation process was observed in the case of chlorine-free arenes over CuY or PdY (16), the substitution of Cl may be considered as the cause of deactivation. As previously mentioned, chlorocompounds are known to be among the most effective catalyst poisons (27). At a first glance, blocking of the metal cations by Cl seems to be a plausible explanation for deactivation. Indeed, for PdY a Pd–Cl interaction could be detected by means of EXAFS/XANES, but direct blocking is probably not the cause of the poisoning, as the Pd–Cl interaction vanishes after deactivation. In the case of PdHY a direct Pd–Cl coordination could not be observed (32). Moreover, if metal–Cl interaction were too strong, no transchlorination should be observed.

Not only is the presence of Pd within the zeolite primarily responsible for the oxidation reaction, although NaY is not completely inactive (16), but Pd is also thought to act as a chlorinating agent, especially when proton-free PdY is used for CBz oxidation. In the literature $PdCl_2$ (34) is reported to

TABLE 3

Influence of the Temperature and the Oxygen Concentration on Conversion and Product Yield for C_6H_5Cl Oxidation over PdHY-2.0

			Products (mol%)						
T (K)	$c(O_2)$ (vol.%)	Conv. (%)	HCl	C_6H_6	$C_6H_4Cl_2$	$C_6H_3Cl_3$	$C_6H_2Cl_4$	C_6HCl_5	C_6Cl_6
573	20	98	10	<0.01	<0.01	0.07	2	2	0.6
673	20	100	40	n.d.	n.d.	n.d.	0.05	0.6	0.4
673	40	100	40	n.d.	n.d.	n.d.	n.d.	<0.01	<0.01

Note. Limit of quantification ca. 0.01 mol%; TOS = 6 h; $V_{cat} = 1.5$ ml; $F = 60$ ml/min; $\tau = 1.5$ s; $m_{cat} = 7.7$ g.

have a chlorinating effect on aromatic compounds. When benzene and dichlorobenzene react with each other over $PdCl_2/C$, the formation of CBz has been observed (35). Bearing this in mind, we assume that formation of a chlorinated coke is responsible for deactivation. This coke-(Cl_n) species, which might cover active centres, is believed to be much more resistant to oxidation than unchlorinated coke. The important role which coke plays in the zeolite-catalyzed combustion of arenes such as benzene has been recently established (36).

As mentioned above, deactivation could be suppressed by raising the catalyst temperature. However, the yield of transchlorination products, viz. polychlorinated benzenes, increased simultaneously. The introduction of protons into the zeolite lattice led to a lower PCBz yield. Thus the formation of HCl is accelerated, but a complete suppression of transchlorination could not be achieved. Obviously lattice protons able to bind Cl as HCl are irreversibly consumed during the oxidation reaction. Addition of H-rich compounds such as *m*-xylene to the feed does not suppress transchlorination, suggesting that lattice protons are not restored by the conversion of H-rich substrates.

The positive effect of high O_2 concentration in decreasing PCBz formation (Table 3) may be explained in the following way. Chlorine and oxygen compete with each other for the active sites. In the presence of excess oxygen, the active centres responsible for transchlorination in PdHY are chiefly occupied by oxygen.

The so-called Deacon equilibrium

$$4\,HCl + O_2 \rightleftharpoons 2\,H_2O + 2\,Cl_2$$

favors Cl_2 formation up to a temperature of about 860 K. It should be noted that in no case was Cl_2 evolved, regardless of the reaction conditions applied. This result seems surprising as within the temperature range used Cl_2 should be thermodynamically favored over HCl. Also an excess of oxygen should have the same impact on the state of the Deacon equilibrium. From this we conclude that the reactants follow different reaction pathways during catalytic reaction compared to those available in the case of thermal reaction. An explanation at the molecular level may be the following. No chlorine species that are able to combine with each other (Cl radicals or differently charged Cl ions) are formed during reaction on the catalyst surface.

At present it seems to be very difficult to avoid the formation of undesired organic transchlorination by-products when using Pd-containing Y zeolite for the catalytic deep oxidation of CBz.

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