Hydrogen–deuterium isotope effects in the reactions of chlorobenzene and benzene on a Pt/γ-Al_2O_3 catalyst

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The kinetic isotope effect for combustion of a C_6H_5Cl/C_6D_5Cl mixture on Pt/γ-Al_2O_3 was found to be close to unity between 520 and 580 K. However, in the presence of an excess of heptane, an isotope effect of 1.5 was found between 460 and 490 K. For the combustion of a C_6H_6/C_6D_6 mixture the k_H/k_D value was around 2 between 404 and 439 K. The results show that in the combustion of chlorobenzene *per se*, C–H bond activation is not a rate-determining step. On Pt sites, C–Cl bond scission probably occurs already at low temperatures. The chlorine and the phenyl group cannot easily react further. Chlorine on the surface is active in chlorination, which is shown by the formation of C_6D_5Cl in an experiment with C_6H_5Cl and C_6D_6. Only at a certain temperature is the chlorine removed, partly as polychlorinated benzenes. The removal of chlorine from the catalyst allows oxygen to take part in the reaction, which determines the rate of the combustion of chlorobenzene. When heptane is present, Cl is removed from the surface and C–H bond scission can become rate determining, as is also the case in the combustion of C_6H_6/C_6D_6. Upon (partial) combustion of C_6H_5Cl/C_6D_5Cl and C_6H_6/C_6D_6 mixtures on a Pt/γ-Al_2O_3 catalyst, hydrogen–deuterium exchange occurs on the γ-Al_2O_3 support.

KEY WORDS: H–D exchange; isotope effect; chlorobenzene; benzene; Pt/Al_2O_3; chlorinated hydrocarbons; combustion

1. Introduction

Catalytic combustion is an emerging technology for the removal of hazardous chlorinated compounds from flue gases. Various (noble) metals have been screened for their catalytic activity, and in most cases serious drawbacks were encountered, such as rapid deactivation [1,2], or simultaneous production of toxic by-products [3–6]. Combustion of chlorobenzene using platinum on γ-Al_2O_3, for example, was found to produce considerable amounts of polychlorinated benzenes [7].

In this study, the competitive combustion of chlorobenzene and its perdeuterated analog on a 2wt% Pt/γ-Al_2O_3 catalyst is investigated. Determination of the kinetic deuterium isotope effect is instrumental to gain more knowledge as to the heterogeneous interaction of chlorinated compounds with catalytic surfaces [8].

Hydrogen–deuterium exchange reactions with C_6H_5Cl/C_6D_5Cl, as well as with C_6H_6/C_6D_6, on Pt/γ-Al_2O_3 and on the γ-Al_2O_3 support alone have also been explored. H/D exchange reactions in various catalytic conversions of benzene have been reviewed in the past [8,9].

2. Experimental

The 2% Pt/γ-Al_2O_3 catalyst was prepared from $H_2[Pt(OH)_6]$ (Johnson Matthey) and γ-alumina (Degussa C) by homogeneous deposition precipitation (for details, see [7]). The catalyst was calcined in air at 873 K. Examination of the catalyst with transmission electron microscopy (TEM) yielded a mean Pt crystallite size of 8 nm. The particle size distribution was rather large: the 95% statistical confidence limit was 6 nm. This mean crystallite size corresponds with a dispersion of 12.5% [10]. The dispersion determined by CO chemisorption was 15.5%. An explanation for this discrepancy could be that small Pt crystallites could not be observed by TEM (enlargement 225 000). The BET surface of the 2% Pt/γ-Al_2O_3 catalyst as measured by nitrogen adsorption was 95 $m^2\ g^{-1}$.

The catalyst with a particle size between 150 and 300 μm was placed in a quartz reactor (i.d. = 12 mm, 300 mg catalyst, volume = 6 ml). For each experiment a fresh catalyst was used. The temperature in the catalyst bed was measured by a thermocouple in a fixed insert in the reactor. The composition of the carrier gas was 85% N_2 and 15% O_2, which were introduced via calibrated mass flow controllers. The C_6H_5Cl (Baker analysed), C_6D_5Cl (Acros, 99+% isotopic purity), C_6H_6 (Merck), and C_6D_6 (Acros, 99.5%) were fed by separate thermostat-controlled impingers in concentrations of about 1000 ppm. Ratios of deuterated and non-deuterated compounds were close to unity. Pertinent data are given in the figure captions. The gas hourly space velocity at room temperature was 10 000 h^{-1}. Glass-lined stainless-steel tubing was used to prevent unwanted side reactions. The set-up was regulated and monitored by a software package [11].

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For the H/D-exchange experiments, the temperature was raised slowly in steps of 50 K. At every temperature, and after 30 min equilibration, samples were collected for 30 min in an ice-cooled trap filled with 5 ml of *n*-hexane and a known amount of 1-chlorohexane as the external standard. Analysis was performed on a HP5890 gas chromatograph (Chrompack CP-SIL5 column), equipped with a HP5972 mass selective detector. The mass spectra were corrected for the contribution of carbon and chlorine isotopes, using spectra of samples collected when the catalyst was bypassed. For comparison, experiments with γ-Al_2O_3 (300 mg, BET surface area $= 100\ m^2\ g^{-1}$) and in an unpacked reactor were performed under the same conditions.

For the measurements of the kinetic isotope effect the same instrument was used, but the analysis was performed on-line on a HP 5890 series II GC equipped with a flame ionisation detector (FID) and a Chrompack CP-SIL5-CB column, was operated at the lowest possible temperature (303 K). However, under these conditions, the hydrogenated and deuterated compounds could not be fully separated. Therefore, conversions were calculated using peak heights, instead of the peak areas. Blank runs were recorded at a reactor temperature of 323 K and after 120 min equilibration to avoid effects of selective adsorption of the reactants. Subsequently, with a rate of $2\ K\ min^{-1}$ the next preset reaction temperature was reached, and, after equilibration for 20 min, six GC analyses (15 min each) were performed. Conversions and rates at various temperatures were calculated using the blank runs at 323 K. Reaction rate constants were calculated, accepting first-order plug-flow behaviour, with the space-time τ (s^{-1}) based on the total molar flow speed and the volume of the catalyst. The margins of error in the k_H/k_D values were calculated combining the errors in the average peak heights of the deuterated and non-deuterated compound, in both the blank runs and of the GC runs at elevated temperature.

Fourier transform infrared (FTIR) spectroscopic experiments were performed on a 0.5% Pt/γ-Al_2O_3 catalyst, because it has a better transparency than a catalyst with a 2% Pt loading. The apparatus and procedures have been described before [12]. In short, the disc was placed in a vacuum device and degassed at 623 K, which leaves about 6×10^{14} OH-groups cm^{-2} on the alumina surface [13]. The spectra were recorded on a Nicolet 5DXC FTIR spectrometer. About 1 mbar of C_6D_5Cl was added and after 10 min spectra of the gas phase and the disc were taken. Temperature was raised with $5\ K\ min^{-1}$ to 623 K, and after 30 min the gas phase was evacuated and spectra were taken.

3. Results

3.1. H/D exchange between C_6H_5Cl and C_6D_5Cl

Figure 1 shows the chlorobenzene disappearance (combustion) on the Pt/γ-Al_2O_3 catalyst. At 573 K C_6H_5Cl and C_6D_5Cl are converted for about 50%, and conversion is almost complete at 723 K, in accordance with earlier observations [7]. Some H/D exchange was observed at 523 K. At temperatures above 673 K, amounts of chlorobenzene were too low to monitor the degree of H/D exchange.

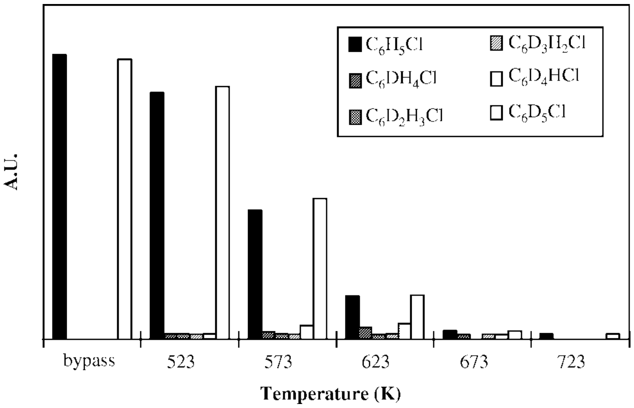

Figure 1. Conversion of, and H–D exchange in, a C_6H_5Cl/C_6D_5Cl mixture on 2 wt% Pt/γ-Al_2O_3. In the bar diagram, the fully hydrogenated molecule is black and the lighter colours of the other bars indicate an increased degree of deuteration. Amounts were corrected for ^{13}C and ^{37}Cl isotopes. Conditions: 500 ppm C_6H_5Cl, 500 ppm C_6D_5Cl, 15% O_2, balance N_2.

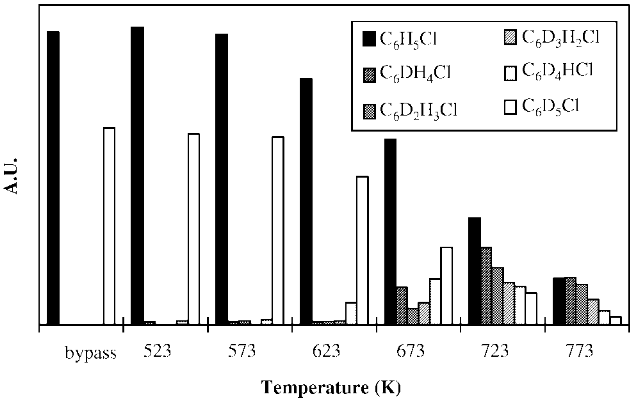

Figure 2. Conversion of, and H–D exchange in, a C_6H_5Cl/C_6D_5Cl mixture on γ-Al_2O_3. Amounts were corrected for ^{13}C and ^{37}Cl isotopes. Conditions: 500 ppm C_6H_5Cl, 350 ppm C_6D_5Cl, 15% O_2, balance N_2.

Above 573 K the formation of polychlorinated benzenes was observed. First, only dichlorobenzenes were found but at higher temperatures also tri- and tetrachlorobenzenes were detected. The chlorination of the 1 : 1 mixture of chlorobenzene and chlorobenzene-d_5 was subject to an isotope effect: at 573 K the dichlorobenzenes (all three isomers) stemming from C_6D_5Cl were only 60% compared to those from C_6H_5Cl. At higher temperatures, H/D exchange hampered the identification of the source of the polychlorinated benzenes.

To examine the influence of the support on H/D exchange, the experiments with C_6H_5Cl/C_6D_5Cl were repeated using only γ-Al_2O_3. As expected, combustion of chlorobenzene was much slower (see figure 2). The H/D exchange occurs above 573 K and the hydrogen-containing isotopomers are more abundant. The concentration of hydrogen species in the system is larger than of deuterium atoms, not only be-

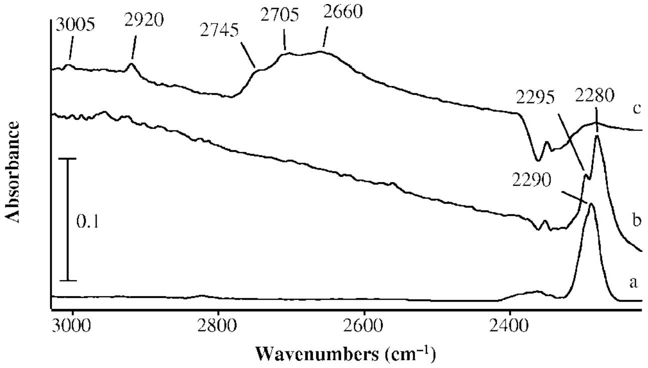

Figure 3. FTIR spectra showing interaction of C_6D_5Cl with 0.5% Pt/γ-Al_2O_3. (a) Gas-phase spectrum. (b) Adsorbed C_6D_5Cl at 298 K, after subtraction of the gas phase (spectrum (a)) and a blank spectrum of the catalyst before introduction of C_6D_5Cl. (c) Upon reaction of C_6D_5Cl at 623 K for 30 min, after evacuation of the gas phase and after subtraction of the blank spectrum. The disturbances in between 2400 and 2300 cm^{-1} are due to CO_2 outside the vacuum device.

cause the initial concentration of C_6H_5Cl is slightly higher than that of C_6D_5Cl, but also because of the hydrogen in the hydroxyl groups of the alumina. The concentration of surface hydroxyl groups on γ-Al_2O_3 depends on the temperature. At 573 K the concentration has been reported to be 7.2×10^{14} OH-groups cm^{-2} [13], which equals $\sim$3.5 $\times$ 10^{-4} mol for 0.3 g of our γ-Al_2O_3 (surface area = 100 $m^2\,g^{-1}$). The total flow of C_6H_5Cl/C_6D_5Cl is around 4×10^{-6} mol min^{-1}, and with a reaction time of several hours, this supplies a mass flow in the same order of magnitude as the amount of surface OH groups.

Comparing figures 1 and 2 makes clear that the H/D exchange is similar on 2% Pt/γ-Al_2O_3 and γ-Al_2O_3 alone. When the same reaction was conducted without any solid material no H/D exchange was observed, which is in accordance with earlier observations [14]. The homogeneous combustion started above 700 K, which means that part of the chlorobenzene combustion in the presence of γ-Al_2O_3 occurs homogeneously in a gas-phase reaction.

The reaction of C_6D_5Cl with a 0.5% Pt/γ-Al_2O_3 catalyst has been studied by FTIR spectroscopy (figure 3). Adsorbed C_6D_5Cl at room temperature (spectrum (b)) shows C–D stretch absorptions at 2295 and 2280 cm^{-1}. The shift compared to the gas-phase spectrum of chlorobenzene-d_5 (spectrum (a)) – a broad peak at 2290 cm^{-1} – is probably due to the effect of physisorption of C_6D_5Cl [12]. The C–D stretch absorptions have disappeared after reaction at 623 K (spectrum (c)); instead some bands are observed in the C–H stretch region, similar to those from C_6H_5Cl when applied at 623 K. A very broad new band has emerged around 2700 cm^{-1}, the O–D stretch region [15]; from its shape this band can be attributed to alumina OD groups [12,13].

These results indicate that all deuterium atoms of C_6D_5Cl have been replaced by hydrogens from the alumina surface. Which is explained by the fact that in the FTIR experiments the concentration of C_6D_5Cl was large compared to the concentration of surface OH groups.

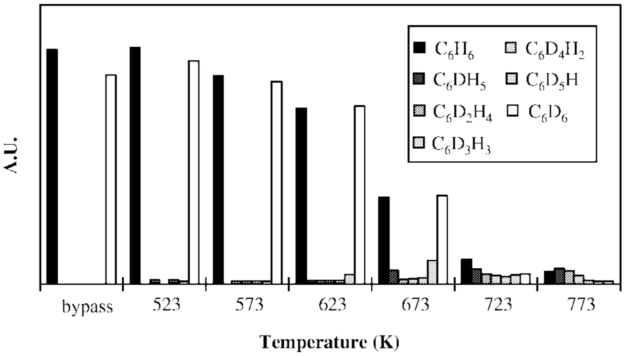

Figure 4. Conversion of, and H–D exchange in, a C_6H_6/C_6D_6 mixture on γ-Al_2O_3. Amounts were corrected for ^{13}C and isotopes. Conditions: 1000 ppm C_6H_6, 900 ppm C_6D_6, 15% O_2, balance N_2.

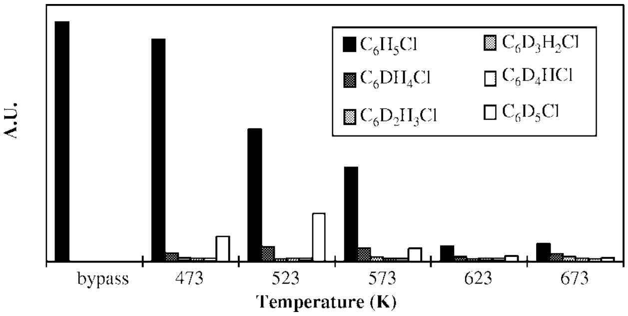

Figure 5. Conversion of, and H–D exchange in, a C_6H_5Cl/C_6D_6 mixture on 2 wt% Pt/γ-Al_2O_3. Amounts were corrected for ^{13}C and ^{37}Cl isotopes. Conditions: 300 ppm C_6H_5Cl, 1500 ppm C_6D_6, 15% O_2, balance N_2.

3.2. H/D exchange between C_6H_6 and C_6D_6

An assessment of the H/D exchange between benzene and perdeuterobenzene on 2% Pt/γ-Al_2O_3 was not possible, because the rate of combustion is much faster. Conversion is complete around 523 K and at this temperature – apart from traces of C_6DH_5 and C_6D_5H – no redistribution was observed. On γ-Al_2O_3 conversion occurred at higher temperatures and H/D exchange started at around 600 K (figure 4). Exchange was slightly less than with the C_6H_5Cl/C_6D_5Cl mixture and conversion of benzene was somewhat faster than that of chlorobenzene. Like with chlorobenzene, at the higher temperatures the hydrogen-containing benzenes were more abundant than the deuterium-containing ones. With an unpacked reactor no H/D redistribution was observed and conversion of benzene started only above 650 K.

3.3. Mixture of C_6H_5Cl and C_6D_6

With a mixture of chlorobenzene and benzene-d_6 on 2% Pt/γ-Al_2O_3, above 473 K C_6D_5Cl was formed (figure 5). The product of formal Cl/D exchange, C_6H_5D, was not found. The H/D exchange in chlorobenzene was higher than for the C_6H_5Cl/C_6D_5Cl mixture (cf. figure 1) due to the rather high concentration of C_6D_6 (1500 ppm, with 300 ppm C_6H_5Cl). The high rate of combustion hampered the quantification of the H/D exchange for benzene-d_6.

Table 1
Kinetic isotope effect in combustion of C_6H_5Cl/C_6D_5Cl on 2% Pt/γ-Al_2O_3.

T (K)	Conv. C_6H_5Cl (%)	Conv. C_6D_5Cl (%)	k_H/k_D[a]
520	7.7	6.7	1.2 ± 0.6
530	14.6	12.2	1.2 ± 0.2
539	19.9	16.6	1.2 ± 0.3
550	28.4	24.0	1.2 ± 0.2
559	37.5	32.5	1.2 ± 0.1
569	42.6	44.7	0.9 ± 0.2
579	53.4	51.1	0.9 ± 0.1

[a] Margins of error for 95% confidence level. Conditions, see section 2.

3.4. Kinetic isotope effect

At modest (<50%) degrees of conversion of chlorobenzene on 2% Pt/γ-Al_2O_3 the isotope effect has been determined. The difference in combustion rate of chlorobenzene and perdeuterochlorobenzene is small (table 1). A k_H/k_D of ca. 1.2 between 520 and 560 K, and 0.9 at higher temperatures (and higher conversions) suggests that, within experimental uncertainties, the kinetic isotope effect remains essentially constant and close to unity. Some changes may occur when diffusion becomes rate limiting, as is often the case at high degrees of conversion. At these temperatures also formation of polychlorinated benzenes became prominent, which could also influence chlorobenzene conversion by blocking adsorption sites. As mentioned earlier, the hydrogen-containing polychlorinated benzenes were more abundant, but exact ratios cannot be given because the chromatographic separation was poor.

In an earlier investigation we found that the addition of heptane to the feed had a remarkable effect on chlorobenzene conversion: combustion rate was increased (temperature for 50% conversion shifted from 290 to 225°C) and by-product formation was suppressed [16]. The kinetic isotope effect was determined for the combustion of C_6H_5Cl/C_6D_5Cl in the presence of an excess of heptane (5000 ppm heptane + 500 ppm of C_6H_5Cl and C_6D_5Cl each). Indeed, chlorobenzene conversion started at lower temperatures than without heptane. Heptane conversion is only 3.5% at 489 K, when about one half of the chlorobenzene is converted (but absolute amounts converted are comparable). The k_H/k_D values were higher than with chlorobenzene *per se*, and the average value of 1.5 is significantly different from unity (table 2).

The kinetic isotope effect for the combustion of a benzene/benzene-d_6 mixture on the 2% Pt/γ-Al_2O_3 catalyst was also studied. At temperatures between 400 and 420 K the k_H/k_D value was around 2 (see table 3). The uncertainties were rather large, but the values are significantly larger than those for chlorobenzene/chlorobenzene-d_5. At higher conversions (>80%) the isotope effect approached unity, which can be caused by the reaction entering a diffusion-controlled regime from a kinetic one.

Table 2
Kinetic isotope effect in combustion of C_6H_5Cl/C_6D_5Cl + heptane on 2% Pt/γ-Al_2O_3.

T (K)	Conv. C_6H_5Cl (%)	Conv. C_6D_5Cl (%)	k_H/k_D[a]
463	15.7	10.4	1.6 ± 0.3
474	25.5	17.8	1.5 ± 0.1
478	34.1	24.5	1.5 ± 0.3
483	41.6	30.4	1.5 ± 0.1
489	51.3	38.8	1.5 ± 0.2

[a] Margins of error for 95% confidence level. Conditions, see section 2.

Table 3
Kinetic isotope effect in combustion of C_6H_6/C_6D_6 on 2% Pt/γ-Al_2O_3.

T (K)	Conv. C_6H_6 (%)	Conv. C_6D_6 (%)	k_H/k_D[a]
404	7.0	2.8	2.4 ± 1.0
409	11	5.2	2.3 ± 0.4
419	46	29	1.8 ± 0.1
439[b]	26	14	2.1 ± 0.4

[a] Margins of error for 95% confidence level. Conditions, see section 2.
[b] A diluted catalyst (30 mg 2% Pt/γ-Al_2O_3 + 270 mg γ-Al_2O_3) was applied.

A clear temperature dependence could not be established. This is illustrated by the k_H/k_D value of 2.1 at 439 K measured with a tenfold-diluted catalyst, which caused benzene combustion to occur at higher temperature.

4. Discussion

4.1. Hydrogen–deuterium exchange

The H/D exchange between aromatic nuclei and their deuterated analogues was found to be fast on many metal surfaces, among which platinum [17,18]. Redistribution of hydrogen and deuterium atoms between C_6H_6 and C_6D_6 was observed on γ-Al_2O_3 as well [19].

The exchange of chlorobenzene with D_2 on platinum has been reported, but C–Cl bond scission and subsequent hydrogenation to (monodeuterated) benzene was found to be much faster [20].

On activated carbon, H/D exchange of chlorobenzene/chlorobenzene-d_5 is slightly faster than of benzene/benzene-d_6 [21], which is in contrast with the results on metal films, where benzene is exchanged much faster than its halogenated analogues [20]. On metal films exchange reaction sites are blocked by dissociated chlorobenzene. This C–Cl bond dissociation probably does not occur on activated carbon and alumina, so other factors (e.g., adsorption of the reactant) determine the exchange rate.

The H/D exchange between C_6H_5Cl and C_6D_5Cl on 2% Pt/γ-Al_2O_3 is in competition with the catalytic combustion reaction. The extent of exchange is very similar when the same reaction is studied on γ-Al_2O_3 alone, however, the rate of combustion is greatly diminished, which suggests that H/D exchange is much more facile on the alumina support than on Pt. This assumption is supported by the formation of aluminium OD groups as was observed by FTIR spectroscopy. Simultaneously, H/D exchange also takes place with the benzene/benzene-d_6 mixture on γ-Al_2O_3. The exchange is somewhat slower than with C_6H_5Cl/C_6D_5Cl, which is in accordance with the literature [20].

Exchange reactions on γ-Al_2O_3 are rather complex and can occur on many different active sites, some of which are poisoned by water, oxygen, and/or carbon dioxide [22]. The reaction of aromatics with alumina can in principle involve an associative (proton addition/proton elimination, the electrophilic substitution mechanism) or a dissociative mechanism, which can occur in two ways. In literature the latter mechanism, involving the heterolytic cleavage of the C–H bond is favoured [13]. Activation of this bond probably occurs on very strong Lewis acid "X-sites" [13,23], and yields a new O–H (O–D) group. Subsequent reaction of, for example, the Al–C_6D_5 species with a neighbouring O–H group yields C_6D_5H.

So, both Lewis acid sites and OH groups (which can be formed by protonation of a basic surface oxygen) are necessary in exchange reactions catalysed by γ-Al_2O_3. The very reactive Lewis acid sites are only exposed after treatment at elevated temperatures (>773 K) [13]. Too high pretreatment temperatures, however, cause the removal of almost all OH groups [24], which leads to zero activity for exchange reactions [25].

Another possibility is protonation of adsorbed aromatic rings, as in common electrophilic aromatic substitution. This reaction is catalysed by acidic materials. This may be of special interest for chlorobenzene, for the HCl formed in the conversion of chlorobenzene can increase the acidity of the alumina. Note that reactions with chlorinated compounds are used to make alumina more acidic [26]. This may be part of the reason – together with a possible better adsorptivity of chlorobenzene – why H/D exchange is faster in a C_6H_5Cl/C_6D_5Cl mixture than in a C_6H_6/C_6D_6 mixture.

4.2. Isotope effect on conversion

The k_H/k_D value for the combustion of the C_6H_5Cl/C_6D_5Cl mixture is not significantly different from unity, so C–H (C–D) bond scission is not involved in any rate-determining step. When the same experiment is repeated in the presence of heptane (and at lower reaction temperature), a k_H/k_D value of ca. 1.5 was found.

This corresponds to a difference in the (free) energy of activation of ca. 1.6 kJ mol^{-1}. In their recent paper, Au-Yeung et al. [27] provide a procedure to calculate the influence of the contributions of the translational, rotational and vibrational partition function differences between molecules and their deuterated analogues. This allows direct comparison to the zero-point energy differences. For C_6H_5Cl/C_6D_5Cl this gives a pre-exponential factor of 0.91, to yield an energy difference of ca. 2 kJ mol^{-1} for combustion of the C_6H_5Cl/C_6D_5Cl mixture in the presence of heptane. The k_H/k_D value for benzene combustion (ca. 2) corresponds to an energy difference of ca. 3 kJ mol^{-1} (with a theoretical pre-exponential factor of 0.95 [27]). This value is closer to the theoretical difference in zero-point vibrational energy (4.8 kJ mol^{-1}) between the C–H and C–D bonds.

So for combustion of benzene and of chlorobenzene in presence of heptane, C–H bond activation is clearly involved in the rate-determining process.

4.3. Reaction of benzene and chlorobenzene with Pt

The data obtained are as yet too limited to allow a detailed mechanistic interpretation. However, it seems that the mechanism of the combustion of chlorobenzene in the presence of heptane (the latter acting as an agent to remove Cl from the surface) approaches that for benzene, where Cl is altogether absent.

The initial π-complex adsorption of both benzene and chlorobenzene yields a strong bond between the π-system and the metal [9,28]. For benzene the next step is the dissociation of one or more C–H (C–D) bonds which allows attack of oxygen [29] – adsorbed on a different type of site than the aromatic compound [30] – or the direct reaction of a C–H (C–D) bond with adsorbed atomic oxygen [9,31]. In both mechanisms C–H or C–D bond activation plays a pivotal role, which explains the isotope effect observed.

The C–Cl bond in chlorobenzene is weaker than the C–H bond in benzene (390 vs. 470 kJ mol^{-1}). Also the bond of Cl with Pt is stronger than of H with Pt [32]. Indeed, C–Cl bond scission has been observed on a Pd(111) surface already at room temperature [33]. However, we have observed that chlorobenzene combustion on Pt/γ-Al_2O_3 takes place at much higher temperatures than benzene combustion. This can be explained by the fact that Cl is a known poison for the oxygen adsorption sites of platinum [34,35]. This results in Cl and a phenyl ring that cannot react further and hence the reaction becomes reversible. The formation of C_6D_5Cl in the experiment with C_6H_5Cl and C_6D_6 is probably due to reaction of adsorbed arene species with chlorine on the surface. Furthermore, the Cl on the surface may also frustrate adsorption of chlorobenzene rings and influence the reaction rate negatively.

Only at higher temperatures (above 523 K under our conditions) is chlorine on the surface removed, partly by reaction with adsorbed phenyl rings to form polychlorinated benzenes. For this chlorination reaction C–H bond activation is involved in the rate-determining step, given the higher amounts of $C_6H_4Cl_2$ compared to $C_6D_4Cl_2$. The removal of Cl probably determines the rate of the reaction.

In the presence of heptane Cl is removed from the surface by the hydrocarbon [16]. This makes the oxygen adsorption sites available again, and causes the combustion reaction to proceed. Carbon–hydrogen bond activation becomes more important, which is reflected by the isotope effect of ca. 1.5 observed.

5. Conclusions

In the presence of oxygen H/D exchange between C_6D_5Cl and C_6H_5Cl and between C_6D_6 and C_6H_6 occurs on γ-Al_2O_3, but when Pt is present, the combustion reaction is much faster. Combustion of a C_6D_5Cl/C_6H_5Cl mixture on Pt/γ-Al_2O_3 is not subject to a significant isotope effect. Probably C–Cl bond scission occurs already at low temperatures, which blocks adsorption sites for oxygen and/or arenes, causing an inhibition of the combustion reaction. Only at a more elevated temperature is Cl removed, which determines the rate of the reaction.

For the catalytic combustion of C_6D_5Cl/C_6H_5Cl in the presence of an excess of heptane an isotope effect of ca. 1.5 is measured. Apparently, C–H (C–D) bond activation now is involved in the rate-determining step of the combustion of chlorobenzene, the heptane serving to remove Cl from the surface.

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