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PLS versus zeolites as sorbents and catalysts
Part 9. An unexpected reaction of Al-PILC sorbed CCl_4 with benzene

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Abstract

Reactivity of CCl_4 on alumina-pillared clays (PILCs) has been exploited to investigate if benzene activation is possible under both static and dynamic conditions. PILC-encapsulated CCl_4 indeed reacts, giving chlorobenzene (PhCl) and biphenyl as main products (with benzoyl chloride as a side-product). Although overall yields are low (2–4%, calculated on starting benzene) they increase when a transition metal-containing pillar is present (e.g. FAZA, which has Fe^{2+}/Fe^{3+}-alumina pillars and activity comparable with the mid-pore zeolite ZSM-5). Yields increase further (e.g. PhCl $> 5\%$) when the PILC is also cation-exchanged, as in Cu-FAZA. Trends in yields on changing reaction parameters show that the reaction giving PhCl occurs via a cation-intermediate, whereas biphenyl is formed via a free-radical mechanism.

Finally, chlorohydroxybenzenes can be obtained in both mid-pore zeolites and PILCs, which is rationalised in terms of generation of active oxygen species at the Lewis acid sites. It is suggested that benzoyl chloride forms from interaction between in situ-generated $COCl_2$ and Lewis acid sites.

Keywords: Heterogeneous catalysis; PILCs; Halogenation; Arenes

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1. Introduction

Intra-zeolite organic chemistry is well-developed [1] as is also ligand encapsulation in zeolites to generate active catalytic sites, whose geometry and charges differ from those of the same complexes in solution [2]. It has been developed for metal complex formation in zeolites ('ship in bottle') [3] and, although to date confined to ligand + complex reactions, also suggested as a means for carrying out chemical reactions of possible industrial importance. [4] Surprisingly, however, there are no cases of zeolite-encapsulated simple organics capable of undergoing ion and radical reactions under constrained, solid state conditions.

During work on pillared clays (PILCs, i.e. smectite clays in which layers are propped apart and cross-linked by nano-oxide pillars to give tuned porosity/acidity materials for sorption and catalysis) it was observed that several retained dichloromethane and chloroform over a wide temperature range (35–450 °C). This suggested PILCs may be useful not only for catalytically destroying retained halocarbons (as described previously) [5,6] but also as 'reaction vessels', in which encapsulated halocarbon (or intermediate derived from it) subsequently reacts with other incoming substrate molecules.

Benzene activation is a good candidate for testing this possibility because although benzene functionalisation is relatively easily reached using mineral acids, in recent years emphasis has been placed on improving the environmental impact of chemical processes, and much work addressed to substituting noxious mineral acids (as well as $AlCl_3$). Prime candidates among the solid acids are zeolites whose many advantages: a crystalline lattice structures, variable pore size and morphologies, and good ion exchange properties, are well-documented. Early attempts at halogenation have included aromatic bromination on/in NaY [7,8] and NaCaX [9] zeolites, and more recently a variety of halogenations of aromatics [10].

However, two limitations are apparent. The first is that the common commercial zeolites have openings smaller than 10 Å and maximum pore diameters which are only slightly larger. Consequently, although some clustering of small molecules is possible inside zeolite pores, volumes are too small to support

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large molecules, which require larger access/egress channels and pore diameters. The second is that the aggressive intermediates formed and the relatively high reaction temperatures involved in gas/solid halogenation reactions in zeolites pose problems of framework stability [11].

We here report reactions of CCl_4 with benzene in a series of PILCs to probe whether they are capable of overcoming these limitations (PILCs are generally more robust in such reactions [12]). Further, during the course of this work, it was also found that both the PILCs investigated and the mid-pore zeolites used as reference standards gave unusual oxidation reactions, leading to possibly useful chloro-hydroxy benzenes, in the latter with no framework stability problems, which constitutes a further point of interest.

2. Experimental

2.1. Materials

The PILCs used were all commercial: BP-PILC, an Al-pillared montmorillonite, from BP Chemicals, AZA and FAZA, respectively an Al- and an Fe/Al-pillared bentonite, from Straton Hi-Tec (Athens). They were chosen because they have been described in detail previously [5]. The popular mid-pore zeolite H-ZSM-5 was used for comparison in two forms with different hydrophobicity: ZSM-5-35 and ZSM-5-235 (35 and 235 are the SiO_2/Al_2O_3 ratios). They were kindly provided by Eutikon, Switzerland. Carbon tetrachloride and benzene were Aldrich products (purity: 99%) and were used as received.

The exchange with Cu(II) was carried out as described previously [13].

2.2. Procedure

In a typical procedure, 100 μL of a selected C_6H_6/CCl_4 mixture were added to 4 mg of catalyst into a 11 mL vial and, after evacuation at liquid nitrogen temperature, heated at a selected temperature. After 4 h the vials were opened and the products extracted from the solid with *n*-hexane. Products were analysed by gas-chromatography on a FID equipped Hewlett Packard 5890 instrument (25 m Carbowax column placed at 50 °C for 15 min and then heated at 10 °C/min to 160 °C and allowed to maintain this temperature for 60 min, $P_{He} = 15$ psi, injector temperature 150 °C, detector temperature 200 °C). Products were then identified by mass spectrometry (Hewlett Packard 5972 Mass Selective Detector equipped with NBS standard database) using the above chromatographic conditions.

Low-contact-time tests were carried out on a SGE Pyrojector as described elsewhere [14].

3. Results and discussion

The gas-chromatograms of the reaction products on FAZA and ZSM-5-235 are presented in Fig. 1. Two different G.C. patterns are obtained. In both reactions, $CHCl_3$, C_6H_5Cl and biphenyl were obtained, but when the PILC was used as a catalyst, benzoyl chloride and isomeric dichlorobenzenes were also formed, while on the zeolite these products were absent and the presence of chlorophenols was observed. In no case was trichloromethylbenzene found among the products.

When a FAZA column was used to obtain chlorocarbon separations a polymeric substance was found on the walls of the detector. Low contact-time tests, on 10 mg of FAZA carried out with an SGE Pyrojector as described in the experimental,

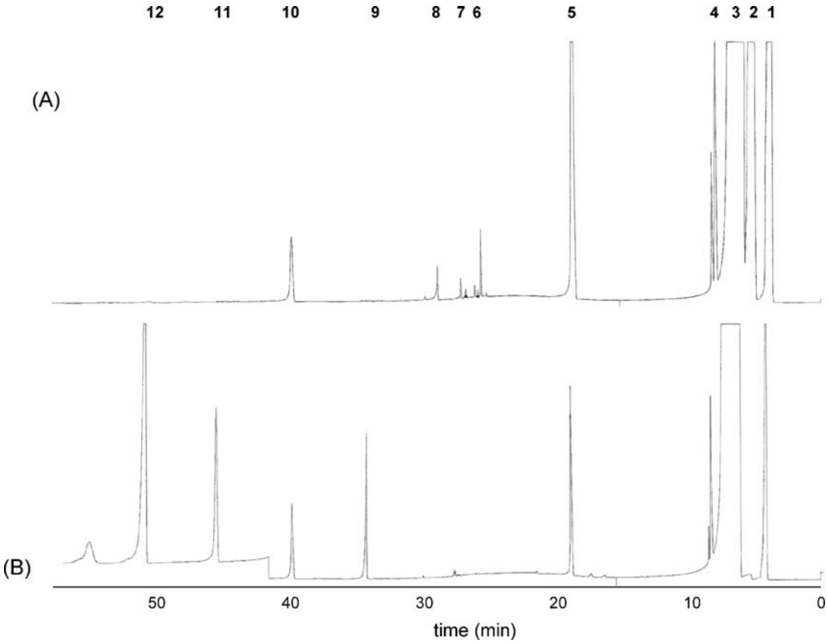

Fig. 1. Gas-chromatograms after 4 h of reaction at 350 °C of 10% CCl_4 in benzene on FAZA (A) and ZSM-5-235 (B). Peaks belong to: (1) *n*-hexane, (2) CCl_4, (3) benzene, (4) $CHCl_3$, (5) chlorobenzene, (6) dichlorobenzene isomer, (7) dichlorobenzene isomer, (8) C_6H_5COCl, (9) Cl–C_6H_4OH GC–MS gave no reciprocal orientation of the Cl and OH groups, (10) biphenyl, (11) dichlorophenol (one of the chlorines is in ortho to the OH group), (12) *p*-chlorophenol.

showed that CCl_4 condensation occurs, due to the presence of C_2Cl_6 as the principal reaction product together with detectable traces of C_3Cl_8 and $COCl_2$ [15]. These results confirm the high reactivity of CCl_4 on this acid catalyst and explain polymer formation in the gas-chromatographic experiments. As previously reported, benzene can be alkylated by alcohols and olefins in PILCs [16] and a mechanism was proposed which involves attack of the alkylating agent on the active site of the catalyst. Given the strong reactivity of CCl_4, we assume it can react with benzene in a similar way. For some catalysts the reaction was carried out for 4 h at 350 °C. The amount of CCl_4 consumed together with the yields of biphenyl and chlorobenzene after this time are reported in Fig. 2.

The overall reaction between benzene and CCl_4 can be represented by:

$$C_6H_6 + CCl_4 \xrightarrow{350^\circ C/4h} C_6H_5Cl + \text{biphenyl} + C_6H_5COCl + C_6H_4Cl_2(\text{all isomers})$$

As shown in Fig. 1, benzoyl chloride and isomeric dichlorobenzenes were formed in minor amounts, but trichloromethylbenzene was not found among the products. Since $COCl_2$ is present among the reaction products of CCl_4 in the absence of benzene and recalling that solid acids can substitute classical Lewis acids (such as $AlCl_3$), formation of C_6H_5COCl is readily explained by the well-known reaction:

$$C_6H_6 + COCl_2 \xrightarrow{\text{Lewis acid}} C_6H_5COCl + HCl$$

Although all yields are low, the formation of chlorobenzenes and especially of biphenyl is intriguing. The first point of note from Fig. 2 is that formation of *both* chlorobenzene and biphenyl is dependent on the CCl_4 percentage in the CCl_4/benzene charge: the higher is the CCl_4% charge, the higher is the yield. Low chlorobenzene yields presumably reflect the wide variety of pore structures of the catalysts studied here (multi-pore in PILCs and PILPs, [17] bent channels in H-ZSM-5 [18]) with consequent diffusion/reaction constraints. With these in mind, two other observations are of interest. Firstly, the highest yield (which occurs at 20% CCl_4) is given for FAZA, i.e. the only PILC having a transition-metal ion ($Fe^{2+,3+}$) containing pillar. This is presumably a reflection of the nature of the pillar. Secondly, the yield is higher on H-ZSM-5/235, i.e. the high SiO_2/Al_2O_3, low-acidity form of the zeolite, than on AZA (the non-iron congener of FAZA). This instead points to greater activity for lower pore acidity and higher hydrophobicity. Together, the conclusion is that the active site in FAZA is the iron-containing pillar.

Secondly, increase in biphenyl yield at higher CCl_4 concentrations is also surprising, because this result instead *excludes* interaction between benzene and catalyst active sites. Indeed, low-contact-time testing on benzene alone carried out up to 370 °C confirmed that biphenyl was *not* formed in these catalyst and temperature conditions. It is established [19] that C–H aromatic bond breaking occurs above 400 °C with generation of free phenyl radicals, which can react with surrounding benzene molecules to give biphenyl [20]. Furthermore, the yield of biphenyl by benzene pyrolysis alone does not reach 1% even at 800 °C [21] and aromatic C–H bond cleavage is only slightly favoured by solid acids above 400 °C. [22] The production of the intermediate phenyl radicals must therefore involve some species formed in CCl_4 decomposition.

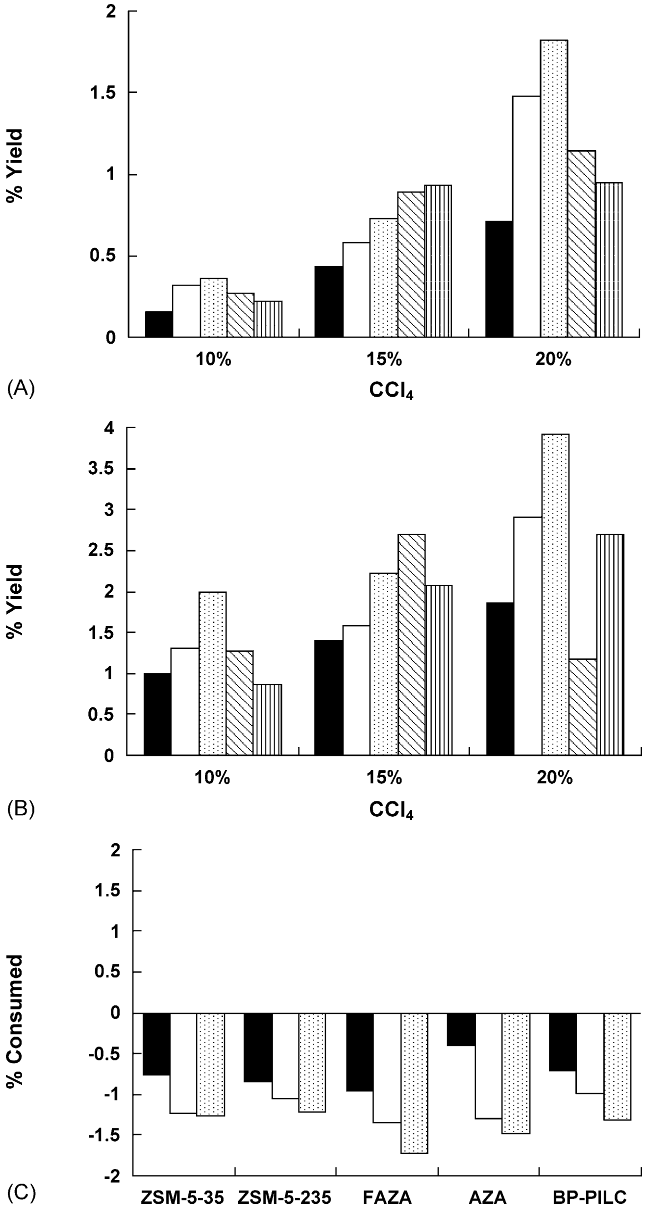

Fig. 2. Yields of chlorobenzene (A) and biphenyl (B) (■, ZSM-5-35; □, ZSM-5-235; ░, FAZA; ▧, AZA; ▥, BP-PILC) and CCl_4 consumption (C) at 450 °C after 4 h (■, 10%; □, 15%; ░, 20% CCl_4).

Two interactions can be postulated between CCl_4 and an acidic site of the catalyst: proton attack at a chlorine atom:

$$\rangle Al{-}O^{-}{-}H{-}Cl{-}{}^{+}CCl_3$$

or proton attack at the carbon atom

$$\rangle Al{-}O^{-}{-}H^{+}{-}CCl_4$$

The first will lead to the formation of a CCl_3^+ cation which should give an electrophilic attack on benzene with formation of $CCl_3–C_6H_5$ as a final (neutral) product (as observed for example in ref. [23]). The absence of $CCl_3–C_6H_5$ among the reaction

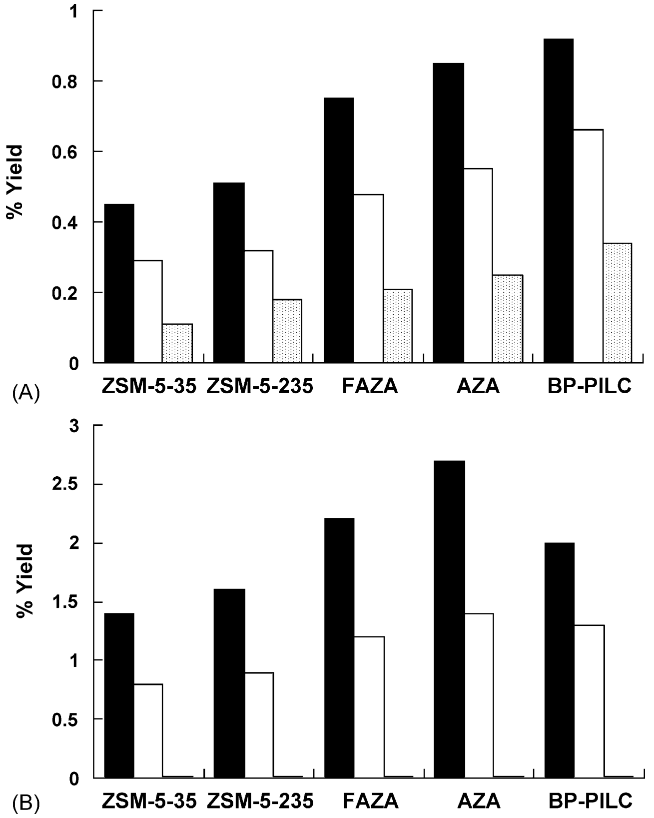

Fig. 3. Product yields of chlorobenzene (A) and biphenyl (B) at different temperatures. (CCl_4 15%, reaction time 4 h) (■, 350 °C; □, 320 °C; ▨, 275 °C).

products found leads us to exclude this mechanism. The second interaction will lead to a positively charged, penta-coordinate carbon (as observed in methane protonation [24]). In turn, this leads to formation of a chloroform molecule and a positively charged chlorine ion (see Fig. 1) the latter then being responsible for chlorobenzene formation. In line with this pathway the higher the concentration of CCl_4, the higher is the number of chlorine ions formed.

On the basis of the results of Fig. 2, the formation of biphenyl can be ascribed to the presence of CCl_4 in the reaction mixture. Obviously, only the interactions between CCl_4 molecules and catalyst active sites are responsible for product formation. This does not mean that there are no interactions between catalyst and benzene. It can be observed that, in the case of HZSM-5 zeolites, increasing the acidity (i.e. lowering Si/Al ratios) decreases the products yields as a consequence of the increase of unreactive interaction between benzene and zeolite active sites, as a consequence of arenium ions formation, occurring also in solid acids. Therefore, a possible mechanism should include a competition between benzene and carbon tetrachloride for the active catalyst site with the complex between CCl_4 and catalyst being the only responsible for product formation [25].

On lowering the reaction temperature, biphenyl and chlorobenzene (Fig. 3) yields decrease, although less for chlorobenzene than for biphenyl, which disappears at 275 °C. This implies a difference in the activation energy of the two reactions, which suggests hydrogen abstraction from benzene of the intermediate.

Also intriguing is the formation of chlorophenols and other oxygenated compounds. In the absence of benzene, $COCl_2$ is present among the reaction products of CCl_4 on PILCs and zeolites and in the absence of CCl_4, benzene gives no reaction. Since this result is obtained in both static (under vacuum) and on-stream experiments, the presence of some reactive oxygen in zeolites and in metal-exchanged PILCs must be postulated. Singlet oxygen atoms are generated on ZSM-5 zeolites at $T > 140$ °C and thermal desorption of such atoms was observed [26]. It is likely that adsorbed molecular oxygen is a precursor of singlet oxygen. Its desorption in the excited state can provoke oxidation reactions. Taking chlorophenols formation first, and limiting discussion to *o*-chlorophenol, i.e. to the oxygenated product obtained in the highest yield, the study was extended to other zeolites, and compared with the ZSM-5s and FAZA.

The results are reported in Fig. 4. It can be observed that Cu-FAZA gives the highest yields of chlorobenzene and biphenyl

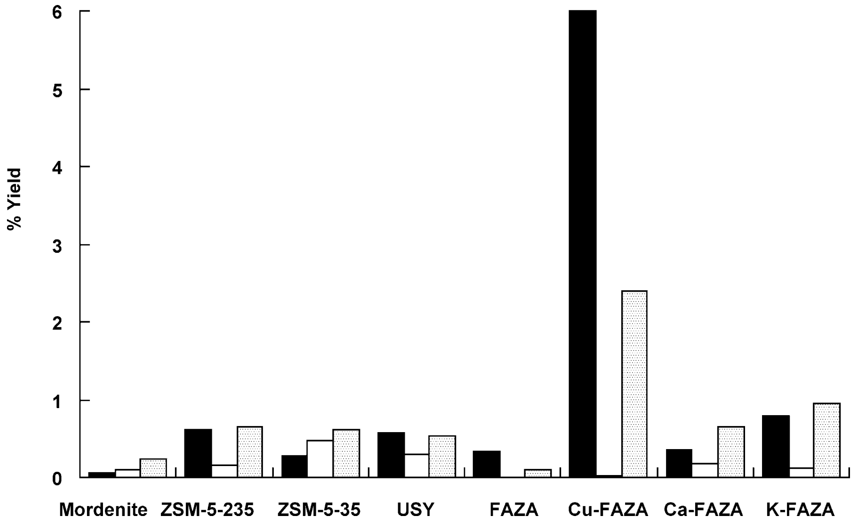

Fig. 4. Reaction products yields of 20% CCl_4 in benzene after 1 h at 350 °C. (■, chlorobenzene; □, *o*-chlorophenol; ▨, biphenyl).

but only a low chlorophenol yield. The other metal-exchanged FAZA catalysts show a similar trend, the lower chlorophenol yields now being comparable with those of ZSM-5-235. Conversely, on increasing the acidity in H-ZSM-5, chlorophenol yields overcomes those of biphenyl.

The H-ZSM-5s were originally investigated as structurally known zeolite standards. However, during the work it was observed that ZSM-5-235 also gives a mixture of *o*-chlorophenol, 1,3-dichloro-4-hydroxy phenol and 1,2-dichloro-4-hydroxy phenol (see Fig. 1). Since these results are apparently the first examples of aromatics oxychlorination in zeolites in the absence of oxygen and under relatively mild conditions, and there was no evidence for zeolite destruction during the reactions, they were extended to zeolites Y and mordenite. As can be seen in Fig. 4, the trend for the *o*-chlorophenol production is ZSM-5/235 > USY > ZSM-5/35 > mordenite in agreement with a reactivity scale already investigated [16].

4. Conclusions

The first point to note is that the PILCs give products different from the mid-pore zeolites. Hydrophobicity more than acidity seems to be responsible for major yields obtained in zeolite experiments (ZSM-5/235 > USY > ZSM-5/35 > mordenite). In PILCs, the reaction yields depend on the pillars, iron/aluminium oxide pillars being more active than alumina pillars (FAZA gives higher product yields than does AZA). Metal-exchange in PILCs provokes an increase in activity. In particular Cu-exchanged FAZA is >10 times more active than FAZA.

However, the spectrum of products is similar for all the catalysts used and indicates that the same intermediate is formed by the attack of CCl_4 molecules on the catalyst active site, probably the pillar. The subsequent ionic reaction leads to benzene chlorination, while the formation of biphenyl can be ascribed to a radical process, following hydrogen abstraction from a benzene molecule by the intermediate.

The formation mechanism of oxidation products, mainly observed in ZSM-5, can be ascribed to singlet oxygen formation. Further studies will clarify this point and, hopefully, how it is generated.

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