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Ship-in-a-bottle synthesis of triphenylamine inside faujasite supercages and generation of the triphenylamminium radical ion

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Abstract—The ship-in-a-bottle synthesis of triphenylamine encapsulated within basic X zeolite has been accomplished by reacting sodium diphenylamide with bromobenzene in the presence of a bifunctional palladium (Hartwig–Buchwald conditions). The presence of incarcerated triphenylamine was demonstrated by dissolving the zeolite with concentrated HF and analyzing the organic material in the dichloromethane extract. Laser flash photolysis (266 nm) gives rise to the generation of triphenylamininum radical cation detected as a transient species decaying in hundreds of microseconds. Upon repetitive cyclic voltammograms, zeolite encapsulated triphenylamine shows a reversible oxidation–reduction process. In contrast, in solution triphenylamine undergoes irreversible oxidation with the formation of coupling dimers.

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1. Introduction

Nowadays, the ability of acid zeolites to generate organic radical cations is very well established,^{1,2} and there is only certain controversy on the nature of the zeolite electron accepting sites. However, it turned out that the initial report of the ability of zeolites to generate radical cations was not very fortunate since none of the two selected probes, 1,1 diphenylethylene and triphenylamine (**Ph**₃**N**), do really generate radical cation within the internal space of the zeolite micropores. The blue species generated upon adsorption of 1,1 diphenylethylene is in reality a dimeric carbocation^{3,4} and on the other hand, it was demonstrated that triphenylamine is not able to penetrate inside the micropores of zeolites, since its molecular size is too large to cross zeolite micropore apertures.⁵

For tridirectional, large pore zeolites whose internal micropore system is formed by larger cavities interconnected by smaller openings, a situation can be envisioned in which a large guest can be accommodated inside the cages, but cannot be adsorbed from the exterior. In these cases, it is sometimes possible to devise a socalled 'ship-in-a-bottle' synthesis in which the final molecule is prepared inside the cages by reacting smaller precursors.^{6,7,8–11} After the synthesis, the large molecule remains 'mechanically entrapped' and incarcerated inside the cavity with some restricted conformational mobility. Herein, we report a ship-in-a-bottle synthesis of triphenylamine inside the cavities of zeolite Y ($Ph_3N@Y$) and the photoinduced generation of its amminium radical cation. Given the historical importance of Ph_3N in zeolite science as well as the use of triarylamminium radical cations as initiators for radical cation chain reactions,¹² particularly Diels–Alder cycloadditions, the feasibility to prepare Ph_3N encapsulated inside zeolites could open future applications of these solids in radical ion chemistry.

2. Results and discussion

The ship-in-a-bottle synthesis of Ph_3N inside zeolite Y was initially attempted by mimicking the reported Ullmann reaction of diphenylamine and iodobenzene in the presence of Cu-containing Y zeolite using potassium carbonate as a base.¹³ However, although different conditions were studied in which the copper oxidation state, temperature, solvent and reaction time were varied, the percentage of Ph_3N formed as detected in the organic solvent was low and significant amounts of unreacted diphenylamine remained. The best results have been obtained using $Cu^{2+}-Y$ (70% Na^+ -to- Cu^{++} exchange) in nitrobenzene at 200 °C, in

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where analysis of the solvent demonstrates the presence in the solution of Ph_3N with 30% of yield. Probably some in situ reduction of Cu^{2+} to Cu^+ occurs during the reaction conditions and this Cu^+ is presumably the active species. IR spectra of the zeolite wafers after the synthesis were complicated due to the presence of residual nitrobenzene or derived products, but anyway these IR spectra conclusively ruled out the presence of Ph_3N inside the zeolite.

Recently, it has been reported a novel Pd-catalyzed procedure for the arylation of amines known as the Hartwig–Buchwald reaction.^{14,15} The main advantages of this methodology are the milder reaction conditions and the excellent yields that are generally obtained. In order to test if this reaction can serve to effect the ship-in-a-bottle synthesis of **Ph₃N**, we prepared a Pd-containing basic X faujasite by adsorbing PdCl₂ on KX zeolite from aqueous solution according to the so-called incipient wetness procedure. For precious, noble metals impregnation with their salts is a common less costly alternative to conventional ion exchange. This bifunctional catalyst (noble metal and basic sites) has been earlier found to be an efficient catalyst for the heterogeneous Suzuki reaction,¹⁶ mechanistically related to the amine arylation needed here to synthesize **Ph₃N**.

Thus, treatment of diphenylamine with sodium *tert*butoxide renders the corresponding diphenylamide anion. By reacting a suspension of this anion with bromobenzene as solvent at 156 °C using PdCl₂–KX as catalyst, the presence of **Ph₃N** was observed in the organic solution as the only detectable product accompanied by the complete disappearance of diphenylamine. Solid–liquid extraction of the solid also leads to the recovery of extra amounts of **Ph₃N** in the absence of any diphenylamine. In a blank control without performing any reaction it was determined that over 70% of the adsorbed diphenylamine is recoverable from PdCl₂–KX by simple solid–liquid extraction, thus, it is reasonable to assume that unreacted diphenylamine could have been detected by our reaction procedure.

Normally in the ship-in-a-bottle methodology, analysis of the liquid phase leads to a product distribution that does not differ much or is compatible with the organic material entrapped inside the solid.⁷ Therefore, analysis of the supernatant constitutes a rational approach towards the understanding of the organic adsorbate encapsulated inside the zeolite pores.¹⁷ Once the product distribution in the liquid phase is compatible with the formation of the Ph₃N and the complete disappearance of diphenylamine is observed, we proceeded to study the solid by diffuse reflectance UV-Vis and IR spectroscopies. In the diffusereflectance UV-Vis spectrum, the Ph₃N@PdCl₂-KX solid exhibits absorption bands at 255 and 315 nm (Fig. 1). The bands are, however, much broader than those recorded of the same compounds in solution, probably indicating the influence of steric constraints, interaction with the zeolite host and/or inhomogeneity in the distribution of **Ph₃N**. The IR spectrum of Ph₃N@PdCl₂-KX exhibits the vibration bands characteristic of the phenyl rings at 1600 and 1495 cm^{-1} (Fig. 2). None of these features appear in the UV-VIS or IR spectra of PdCl₂-KX blank zeolite and they



Figure 1. Diffuse-reflectance UV–Vis spectra of $Ph_3N@PdCl_2-KX$ (spectrum a) and $Ph_2NH@PdCl_2-KX$ (spectrum b). For the sake of comparison the inset shows the UV–Vis spectra of Ph_3N (spectrum c) and Ph_2NH (spectrum d) recorded in dichloromethane.



Figure 2. IR spectra of the samples $Ph_2NH@PdCl_2-KX$ (a) and $Ph_3N@PdCl_2-KX$ (b) recorded at room temperature in a sealed cell after outgassing at 100 °C during 1 h at 10⁻² Pa.

are attributable exclusively to the organic guest formed during the Hartwig–Buchwald reaction.

However, given the similarity between the spectra of diphenylamine and Ph_3N , firm spectroscopic evidence for the formation of Ph_3N and the absence of diphenylamine could not be obtained, since the spectra are compatible with any of the two compounds or a mixture of both. For the sake of comparison, Figures 1 and 2 also contain the spectra of blank controls in which diphenylamine was adsorbed on PdCl₂–KX. Nevertheless, the above spectra, and particularly the IR spectrum of $Ph_3N@PdCl_2–KX$, exclude the presence of some adventitious by-products.

To obtain a conclusive evidence for the presence of $\mathbf{Ph_3N}$ inside the X zeolite, we proceeded to dissolve the aluminosilicate host with concentrated HF and extracted the resulting organic material with CH₂Cl₂ after neutralization with Na₂CO₃. Faujasite X is a suitable zeolite for this type of study, since its aluminosilicate framework easily dissolves in aqueous acids. This experiment served to demonstrate definitely the presence of $\mathbf{Ph_3N}$ in the solid without being able to detect diphenylamine in the extract. This result is compatible with the indirect analytical and spectroscopical data obtained for the supernatant during Download English Version:

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