Characterization of Persistent α,ω-Diphenyl Substituted Allyl Cations within Monodirectional Acid Zeolites

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Two α,ω-diphenyl substituted allylic cations are generated within ZSM-5 and mordenite as persistent species by adsorption of 1-acetoxy-1,3-diphenylpropane and 1,5-diacetoxy-1,5-diphenylpentane onto the H$^+$-form of these zeolites; the diffuse reflectance spectra of these highly coloured samples (orange or pink) matches the very characteristic absorption spectra of these allyl cations in homogeneous solution; the non-acidic Na$^+$-form of these zeolites does not have the same effect.

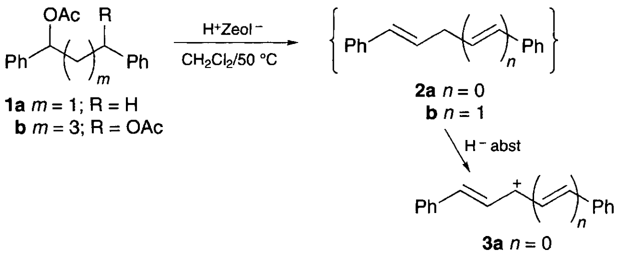
Zeolites are widely used as heterogeneous acid catalysts, both for the synthesis of fine chemicals[1,2] as well as for large-scale industrial petrochemical processes of huge economic importance.[3] Although many of these reaction mechanisms are still poorly understood, it is generally accepted that they must involve the intermediacy of carbenium-like species. Spectroscopic evidence has however revealed that simple alkyl carbenium ions do not exist as a free species but are bonded to the framework oxygens as alkyloxonium ions.[4] A much higher stability is required in order to observe a cation as a persistent free species in the interior of zeolite voids.

Recently, controversial reports have appeared concerning the existence of the unsubstituted parent allyl cation as a free ion after adsorption of allylic alcohol on ZSM-5. Initial assignment of the ^{13}C NMR spectra obtained to the allyl cation[5] have later been found to be due to protonated propanal, diallyl and surface allyl ethers.[6,7] Evidence for the existence of allylic cations as free ions within zeolites has still not been obtained.

Here we show that α,ω-diphenyl substituted allylic cations can exist as persistent free species by adsorption of appropriate neutral precursors onto acid monodirectional zeolites of medium and large pore size.

Commercially available zeolites were used in this work (mordenites, PQ) or were synthesized by hydrothermal treatment according to reported procedures (ZSM-5).[8] Their H$^+$-form was obtained by thermal decomposition (550 °C, overnight) of the NH_4^+ or Me_4N^+ exchanged samples for mordenite and ZSM-5 respectively. Adsorption of 1-acetoxy-1,3-diphenylpropane **1a** or 1,5-diacetoxy-1,5-diphenylpentane **1b** onto dehydrated zeolites (500 mg) was carried out by stirring magnetically a CH_2Cl_2 solution (25 ml) of **1** (25 mg) for 3–6 h at 323 K. The suspensions were then filtered and the solids submitted to continuous solid–liquid extraction, dried and stored in sealed vials. Analyses of the reaction mixtures recovered after extraction (GC-MS) revealed that the starting acetates **1** had decomposed to a large extent during the adsorption to give predominantly olefinic products. The amount of organic material retained on the solids was determined by combustion elemental analysis. The loading values were typically between 1–3 mass%.

Most surprisingly, the alternative procedure of grinding dehydrated zeolite and acetates **1** in a mortar at room temperature without any solvent was also a highly efficient method for the incorporation of organic guests into zeolites.



While with the Na$^+$-exchanged zeolites the solids remained colourless, with the acid zeolites the solids developed during the adsorption procedure the characteristic colour of the corresponding α,ω-diphenyl substituted allylic cation. When incorporation was performed by diffusion without solvent, sample colouration took much longer before it was detectable. However, the intensity steadily increased for a period of weeks to finally give much stronger coloured composites than those prepared by refluxing in CH_2Cl_2. This dry procedure of generating the intermediates **3a,b** at room temperature was very convenient for following the development of the allyl cations from their corresponding starting materials by recording the changes occurring in the diffuse reflectance (DR) spectra of the samples at various times over several days (Fig. 1).

In fact, steady diffuse reflectance of these host–guest systems exhibited an absorption band at λ_{max} 500 and 550 nm after the adsorption of compounds **1a** and **1b** respectively (Fig. 2). These peaks and their shapes perfectly matched those reported for cations **3a** and **3b** in solution, which possess a characteristic shoulder in the blue side of the absorption.[9,10] For both cations, ZSM-5 as a host always gave samples with more intense diffuse reflectance than mordenite. Moreover, while for the ZSM-5 samples the colour did not decrease for periods longer than several months, in the case of mordenite an appreciable fading was observed. Decolouration on mordenite host was particularly rapid for cation **3a** which decayed within several hours, making the characterization of this composite uncertain.

The FTIR spectra of the samples were also compatible with the formation of cations **3**. Fig. 3 shows the aromatic region of the **3b**–HZSM-5 composite after H_2O evacuation at 473 K and 10^{-2} Pa for 2 h. Besides the total disappearance of the strong

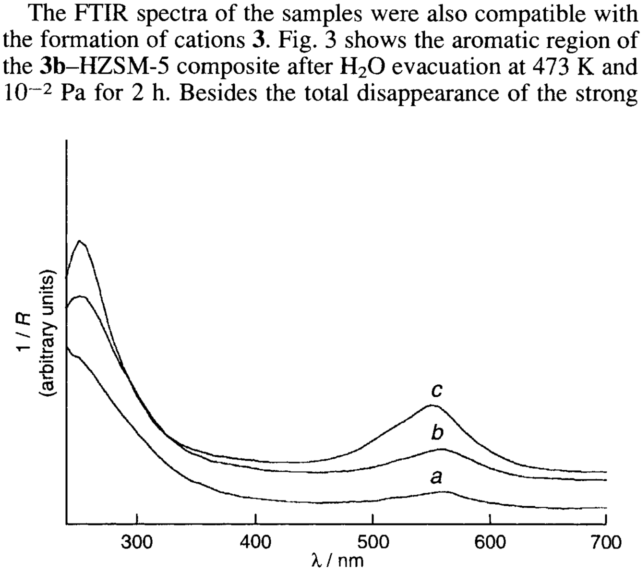


Fig. 1 Diffuse reflectance (inverse of reflectivity, 1/*R*) of compound **1b** incorporated within HZSM-5 at room temp. without solvent. Immediately after the adsorption (curve *a*), 2 days (curve *b*) and 3 weeks (curve *c*) later.

absorption band owing to the carbonyl groups of the starting compound **1b**, the most noticeable feature was the presence of a strong band a 1545 cm^{-1} that is characteristic of these allyl cations. The **3a**–HZSM-5 composite exhibited the same intense absorption at 1550 cm^{-1}. It is worth noting that the intensity of these bands did not decrease after outgassing at increasing temperatures up to 573 K for cations **3a** and **3b**, respectively. This observation indicates that the organic guests are strongly adsorbed on the solid surfaces. This behaviour is characteristic of positively charged species.[11]

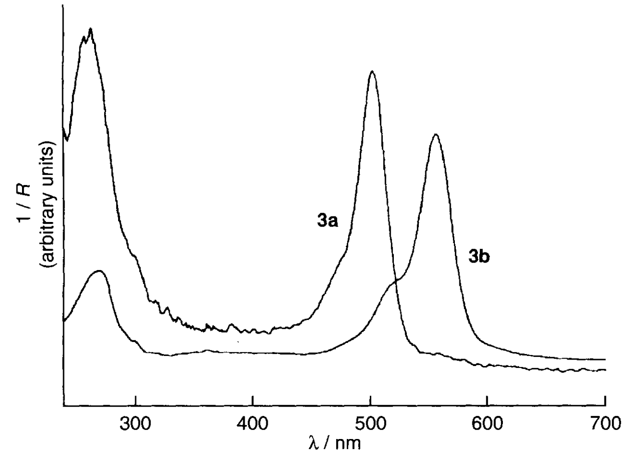


Fig. 2 Diffuse reflectance (inverse of reflectivity, 1/*R*) of cations **3a** and **3b** included within HZSM-5

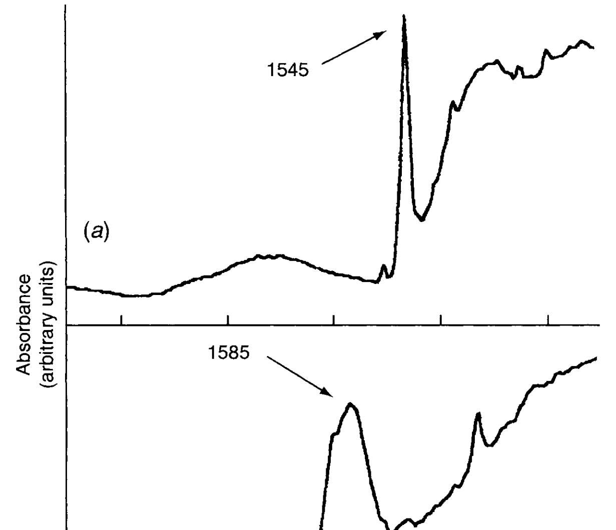


Fig. 3 (*a*) The FTIR spectrum (1800–1400 cm^{-1} region) of cation **3b** absorbed within HZSM-5 (self-consistent wafers, 10 mg) after outgassing at 473 K and 10^{-2} Pa for 2 h. (*b*) Same zone of the FTIR spectrum corresponding to the adsorption of **1b** onto a non-acidic NaZSM-5 (Diffuse reflectance identical to curve a of Fig. 1). The baseline of both spectra has been corrected to reduce the broad absorption band owing to the ZSM-5 framework between 1750 and 1560 cm^{-1}.

By contrast, the IR spectra obtained after similar outgassing of compounds **1a,b** adsorbed on the non-acidic, Na$^+$-form of ZSM-5 (where diffuse reflectances of these white powders did not correspond to any cation) did not exhibit this characteristic 1545 cm^{-1} band [Fig. 3(*b*)], but a different broad band peaking at 1585 cm^{-1} presumably due to the diene precursor **2a,b** or some derivative.

Formation of these cations must involve acetic acid elimination followed by hydride abstraction from the intermediate hydrocarbon **2**. Independently synthesized 1,5-diphenylpenta-1,4-diene (**2b**)[12] was adsorbed onto NaZSM-5 and HZSM-5. In the latter zeolite, clean formation of the cation **3b** occurred, as evidenced by DR (strong 550 nm absorption) and FTIR (1545 cm^{-1}). These spectra (not shown) were identical to the corresponding traces in Figs. 1–3. The signals obtained in the case of the NaZSM-5 sample were very weak, but there was no cation-characteristic band (1545 cm^{-1}) in the FTIR spectrum. Moreover, the neutral diene precursor **1b** exhibited completely different spectra: a single absorption at 275 nm in the UV and two bands at 1598 and 1494 cm^{-1} in the FTIR.

Related precedents about the generation of highly stabilized benzylic cations from the corresponding hydrides by adsorption on acid solids are well documented in the literature.[13,14] The presence of acid sites is a requirement for the success of the overall process, as evidenced by the lack of detectable carbocation generation on the neutral Na$^+$-form of these zeolites. Differences on the relative stability of **3a** and **3b** can explain why the formation of the former is sluggish, desorbs at lower temperatures and decays more rapidly (especially in mordenite), while cation **3b** is readily formed in both zeolites where it is apparently stable for several months.

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