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Surface photochemistry: Ketones included within a channel type solid support, the aluminophosphate $AlPO_4$-5

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Abstract

Diffuse reflectance and laser-induced techniques were used to study the inclusion of an aromatic ketone, benzophenone (BZP) and also of aryl alkyl ketones such as β-phenylpropiophenone (β-PP) and γ-phenylbutyrophenone (γ-PB) into a channel type solid powdered substrate, the aluminophosphate $AlPO_4$-5. $AlPO_4$-5 solid support exhibits a surprisingly hydrophilic character which was shown by a blue shift of the (n,π^*) ground state absorption band of BZP and a red shift of the (π,π^*) ground state absorption band of γ-PB, when compared with the inclusion within silicalite, a hydrophobic support. Furthermore, the phosphorescence emission of BZP within $AlPO_4$-5 was broad and a non-structured emission band of hydrogen bonded BZP centred about 440 nm was observed in a nanosecond time scale. This emission shifts up to 470 nm and was assigned to protonated excited BZP, $BZPH^{+*}$, suggesting the presence of Brönsted acid sites in the substrate. In the 7.3 Å diameter aluminophosphate's channels, β-PP shows no room temperature phosphorescence as consequence of intramolecular quenching, while the larger γ-PB exhibits a structured phosphorescence emission peaking at 452 nm. A lifetime distribution analysis for BZP/$AlPO_4$-5 case shows a single wide band, peaking at 630 μs. The transient absorption spectra of argon purged samples revealed, superimposed on the triplet–triplet absorption of BZP, the hydroxyl–benzophenone radical ($BZP^{\bullet}OH$) absorption as the main transient species in the millisecond time scale.

Keywords: Surface photochemistry; Benzophenone; β-Phenylpropiophenone; γ-Phenylbutyrophenone; Aluminophosphates substrates; Diffuse reflectance; Laser induced luminescence; Flash photolysis; Lifetime distribution analysis

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1. Introduction

Photochemical studies in organized media use the substrate to modify the photochemical and photophysical behaviour of well-known included guest molecules, as a strategy to characterize that substrate. Absorption and photoluminescence spectra measurements on adsorbed molecules provide useful information on the physical and chemical nature of the adsorption sites or surfaces. Carbonyl compounds, namely aromatic ketones, play an important role in these surface photochemical studies because of the richness of their reactivity that makes them very useful probes for the study of inclusion processes within cavities of solid substrates such as calixarenes [1], cyclodextrins or microcrystalline cellulose [2], channels of different zeolites such as ZSM-5 [3,4] or silicalite [2c,5,6], or onto solid powdered supports like silicas [7].

Among the ketones used as probes for surface studies in restricted media, xanthone, because of the sensibility of its triplet–triplet absorption to medium polarity [6c,8,9] and β-phenylpropiophenone (β-PP), because the information it provides about the limitations to conformation interconversion imposed by the internal structure of the host

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[1b,10], are largely referred. Benzophenone (BZP) is also an extremely useful molecule for probing new hosts. The n → π* transition is known to be very sensitive to the nature of the environment and also exhibits a photochemistry which depends on the properties of the host [1c,2c].

Aluminophosphates ($AlPO_4$'s) are class of microporous materials in which alternating AlO_4^- and PO_4^+ tetrahedra are linked together via bridging oxygen atoms forming microporous structures [11]. In contrast to the aluminosilicate zeolites, the $AlPO_4$-5 framework is neutral and non-framework cations are not needed for charge balance. In spite of that, and apparently due to the difference in electronegativity between aluminium and phosphorus, the $AlPO_4$-5 lattice exhibits some hydrophilic character [12]. $AlPO_4$-5 corresponds to AFI structure, consisting of unidimensional 12-, 6- and 4-membered ring channels, parallel and unconnected. The largest channel diameter is 7.3 Å [13]. An interesting feature of aluminophosphates molecular sieves is the ability of the Al framework to coordinate water molecules, forming octahedral framework Al [11,14].

Some recent developments used the possibility of substitution of Al and/or P by Si and also the introduction of metal ions into the framework, generating framework charge and leading to systems with active centres which exhibit catalytic properties [11a,15].

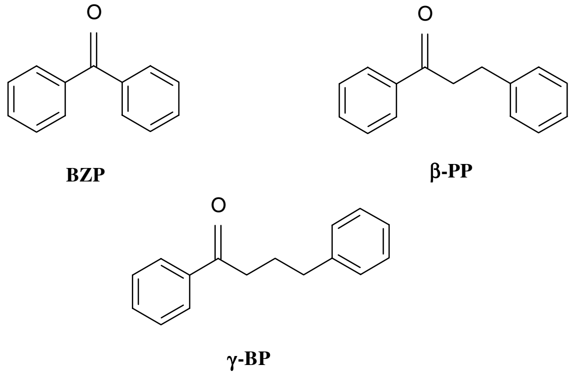
HZSM-5 (MFI structure) is a pentasil zeolite with H^+ as the charge compensating cation. The channel system of this zeolite consists of near-circular zig–zag channels with diameter of 5.4 ± 0.2 Å, which intersect elliptical straight channels with free cross-section of 5.75×5.15 Å. Both channels are defined by 10- membered ring of oxygen ions [16–18].

Silicalite is a de-aluminated analogue of ZSM-5 zeolite. The lack of substitutional aluminium results in silicalite having no catalytic or exchange properties, compared with the ZSM-5 zeolites. Silicalite is the only known hydrophobic form of silica and is capable of adsorbing organic molecules up to about 6 Å of kinetic diameter [2c,6a,19].

The spatial confinement imposed by these pentasil zeolites channels and the different environment they provide to included guests (hydrophilic versus hydrophobic environment), make them, from our point of view, excellent references for comparison purposes of the photochemical studies we performed for BZP within the aluminophosphate $AlPO_4$-5 .

Diffuse reflectance techniques, namely ground-state diffuse reflectance absorption, laser-induced luminescence and diffuse reflectance laser flash-photolysis are very useful means to study opaque and crystalline systems. By the use of these techniques the effect of the host on the photochemical processes experienced by the guest becomes accessible [1,2].

In this study we report the photochemistry of BZP within $AlPO_4$-5 and the results are compared with those obtained for HZSM-5 zeolite and silicalite. The spatial confinement imposed by the aluminophosphate host to the probe is checked by comparison with the laser induced luminescence behaviour of other two probes (Scheme 1), β-phenylpropiophenone and γ-phenylbutyrophenone, included into the aluminophosphate's channels.



Scheme 1. Structure of the ketones used in this study.

2. Experimental

2.1. Materials

Benzophenone (Koch Light, purissimum) was used without any purification. β-phenylpropiophenone and γ-phenylbutyrophenone were from Aldrich and used as received. Hexane and isooctane (Merck, Uvasol grade) were also used as received. Silicalite, from Union Carbide and HZSM-5, Si/Al = 19, from UOP molecular sieves, were used as powdered solid supports. $AlPO_4$-5 was synthesized according to the following procedure.

2.2. Synthesis of $AlPO_4$-5

$AlPO_4$-5 aluminophosphate was crystallized in fluoridric acid medium, using tripropylamine (Pr_3N) as direct-structurating agent. A mixture of the following mole ratio composition was prepared: 1 Al_2O_3/1 P_2O_5/1 Pr_3N/1 HF/50 H_2O. The mixture was stirred 4 h in order to obtain a homogeneous gel. Afterwards the gel was charged into an autoclave and heated at 170 °C under autogenic pressure for 9 h. The solid obtained was recovered by centrifugation, washed several times with distilled water and finally dried overnight at 373 K. As-synthesized $AlPO_4$-5 was calcined to remove the organic template. Typically, 500 mg of powder was heated at 400 °C (5 °C min^{-1}) in N_2 (15 $Lh^{-1} g^{-1}$) for 2 h and then heated at 600 °C (5 °C min^{-1}) in air (15 $Lh^{-1} g^{-1}$) for 8 h.

2.3. Sample preparation

The supports were dried under vacuum, ca. 10^{-3} mbar, at 100 °C for 2 h before use. The solid powdered samples used in this work (50, 100, 250, 500 and 1000 μmol g^{-1}) were prepared using the solvent evaporation method. This method consists in the addition of a solution containing the probe to the powdered solid support. The resulting mixture