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Concept

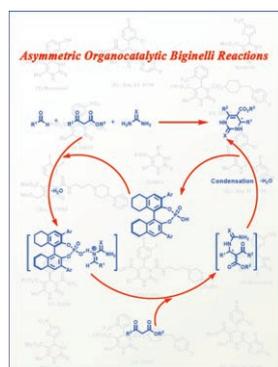
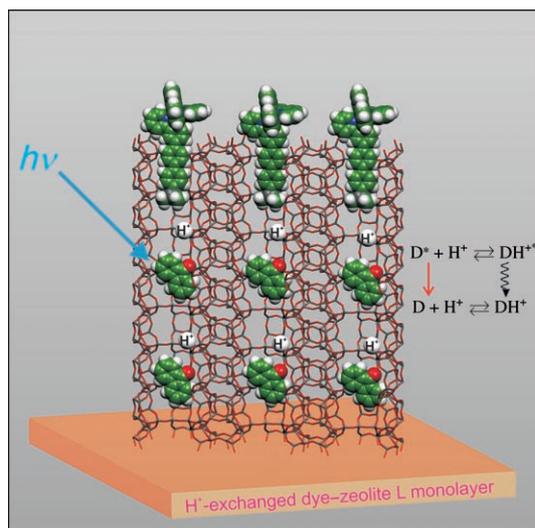
Asymmetric Organocatalytic Biginelli Reactions:
A New Approach to Quickly Access Optically Active
3,4-Dihydropyrimidin-2-(1*H*)-ones
L.-Z. Gong et al.

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Proton activity...

... inside the channels of zeolite L have been studied. In their Full Paper on page 8939 ff., G. Calzaferri and R. Q. Albuquerque described how the systems investigated have been divided into closed, semi-open and open types, depending on the ability to exchange molecules or ions between the channels and the environment. The diagram shows protonation of a dye (OxH⁺) in the ground state and in the electronically excited state. The influence of the proton activity on the luminescence of encapsulated dyes has been discussed in this paper, with special attention being given to luminescence quenching by excited-state protonation.

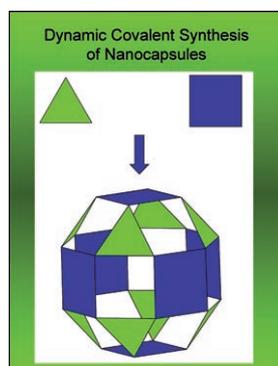
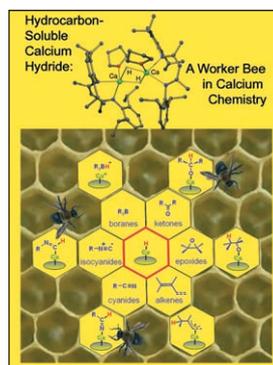


Multicomponent Reactions

In their Concepts article on page 8920 ff., L.-Z. Gong et al. describe the asymmetric organocatalytic Biginelli reaction as a tool to prepare optically active 3,4-dihydropyrimidin-2-(1*H*)-ones in a straightforward and efficient fashion.

Calcium Hydride Complexes

In their Full Paper on page 8928 ff., S. Harder and J. Spielmann describe the reactions of hydrocarbon-soluble calcium hydride complex $[\{\text{CaH}(\text{dipp-nacnac})(\text{thf})\}_2]$ (**1**; dipp-nacnac = $\text{CH}\{\text{CMe}\}\{2,6\text{-iPr}_2\text{C}_6\text{H}_3\text{N}\}_2$) with a variety of unsaturated bonds (alkenes, ketones, cyanides, isocyanides), epoxides and Lewis acids. This is in striking contrast to the reactivity of homoleptic CaH_2 that is essentially inert to these functional groups.



Nanocapsules

In their Full Paper on page 8953 ff., R. Warmuth et al. describe the dynamic covalent synthesis of nanocapsules. The use of two two-dimensional building blocks yields a pure nanocapsule in a high yield. It is predicted that this design principle will be widely applicable to allow the preparation of other nanospheres from different square and triangular building blocks.

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Proton Activity Inside the Channels of Zeolite L

Rodrigo Q. Albuquerque and Gion Calzaferri*^[a]

Abstract: The proton activity inside the channels of zeolite L has been studied by investigating dye-loaded zeolite L crystals under different conditions, such as water content, nature of the counterions, and nature of the solvent. The discussion is made within the frame of three types of dye-loaded zeolite L systems, classified according to their ability to exchange matter (dyes, cations, solvent, and other small molecules) with the environment. The classification refers to dye-loaded zeolites. The term “closed” and “semi-open” characterize different possibilities of

the channels to exchange small molecules, cations, and solvent molecules with the environment, but not dyes. The “open” systems also allow for dye exchange. UV-visible and fluorescence spectroscopy have been used to observe the proton activity inside the zeolite L channels. The influence of the proton activity on the luminescence of encapsulated dyes is discussed, special

Keywords: dyes/pigments • host-guest systems • luminescence • supramolecular chemistry • zeolites

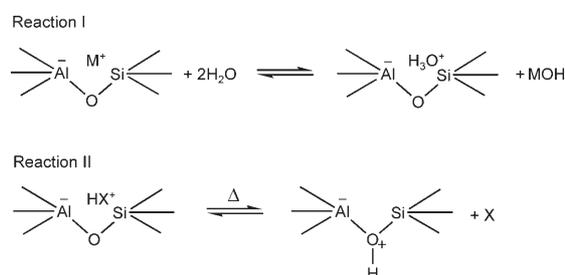
attention being given to luminescence quenching by excited-state protonation. Partially proton-exchanged zeolite L can be a superacid, whereas for the M-exchanged form (M: K⁺, Li⁺, Cs⁺, Mg²⁺, Ca²⁺) the pH ranges from about 2.5 to 3.5. For these last forms, the differences in pH are due to the acid-base reactions of the respective metal cations with water inside the zeolite. Finally, we describe an easy experimental procedure that can be used to tune the proton activity inside the zeolite L to a considerable extent.

Introduction

Zeolites play an important role in petrochemical processes, in which they act as size-selective catalysts in cracking reactions.^[1] The efficiency in catalyzing these reactions stems from their high acidity, which is mainly due to the presence of Brønsted sites. The acid sites are formed after calcination of the zeolite as the protonated H-form is produced. Classical zeolites are built up by corner-sharing TO₄ tetrahedra (T: Si, Al) forming a three-dimensional system of channels and cavities. The substitution of a tetravalent silicon atom by a trivalent aluminum atom in a TO₄ unit generates a negative charge, which is then balanced by a charge-compensating cation. These cations can be completely or partially replaced by means of ion exchange, depending on the type of zeolite, giving rise to a large variety of cation-exchanged zeolites. Hydrolysis and calcination leads to the formation of Brønsted sites as explained in Scheme 1, which shows a simplified view of a zeolite represented by two TO₄ units

and Na⁺, H₃O⁺, and NH₄⁺ as counterions. Brønsted sites are produced by hydrolysis (reaction I), followed by calcination (reaction II).^[2]

Reaction I explains why suspensions of exchanged zeolite crystals in distilled water tend to be basic, whereas at the same time the proton concentration and, therefore, the acidity inside the cavity increases. For example, calcination of zeolite ZSM-5 at 400 °C leads to the highest acidity due to the formation of Brønsted sites, whereas calcination at 700 °C leads to fully hydrated predominance of Lewis acid sites.^[3]



Scheme 1. Schematic representation of a zeolite showing the formation of Brønsted sites through hydrolysis (I) and calcination (II). M⁺ is a charge compensating cation and X: H₂O, NH₃, NH(CH₃)₂, or other small molecules.

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