



Encapsulation of *N,N',N''*-Tricyclohexylguanidine in Hydrophobic Zeolite Y: Synthesis and Catalytic Activity

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Abstract: *N,N',N''*-Tricyclohexylguanidine was encapsulated in hydrophobic zeolite Y by reacting *N,N'*-dicyclohexylcarbodiimide with cyclohexylamine within the supercage. The encapsulated guanidine catalyzes the addition reaction of acetone to benzaldehyde forming 4-phenyl-4-hydroxybutan-2-one as the principal product, as opposed to the homogeneous system which produces 4-phenyl-3-buten-2-one via condensation reaction. © 1997 Elsevier Science Ltd. All rights reserved.

Guanidines are strong non-ionic bases¹ which can be used as catalysts for methylation of phenols and esterification of carboxylic acids,² alkylation of hindered carboxylic acids,³ addition of nitroalkanes to α,β -unsaturated carboxylic esters^{4,5} and transesterification of vegetable oils.⁶ Their heterogenization on organic polymers is possible, but they slowly leach out during transesterification reactions.⁷

In order to circumvent this shortcoming, we have adopted a different approach to heterogenization, namely the synthesis of “ship-in-a-bottle” guanidines by encapsulation in the supercages of zeolite Y. We were able to encapsulate *N,N,N'*-tricyclohexylguanidine (TCG), whose dimensions in the CN_3 plane are 8.7×11.0 Å (determined using the Spartan 4.0 semiempirical program), in Wessalith® DAY[®] (FAU structure) by reacting *N,N'*-dicyclohexylcarbodiimide with cyclohexylamine inside the supercages of this hydrophobic zeolite.⁹ As shown in Fig. 1, the TCG molecule is larger than the channel of the Wessalith®, but small enough to allow its accommodation, together with the substrates, in the supercage whose diameter is 13 Å.¹⁰

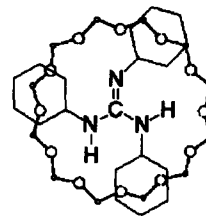


Fig. 1. Graphical representation of TCG in Wessalith®.

Microanalysis shows that 0.42 mmol of TCG per gram of Wessalith® was encapsulated. This value varies slightly in different batches and may reach 0.58 mmol of TCG per gram of Wessalith®, which corresponds to a 60 to 84% occupation of the zeolite Y supercages. If the material is extracted with dry chloroform in a Soxhlet under an inert atmosphere, no TCG is removed. If wet chloroform is used in the extraction, TCG is hydrolyzed to *N,N'*-dicyclohexylurea, which remains in the zeolite, as shown by the IR band at 1636 cm^{-1} . The ^{13}C MAS NMR spectrum of the encapsulated TCG shows four signals (24.5, 25.9, 30.9 and 50.6 ppm) which are only slightly shifted compared to free TCG (25.2, 25.9, 34.2 and 52.5 ppm). The infrared spectrum of the encapsulated TCG shows shifts of the $\nu\text{ C=N}$ double bond from 1615 cm^{-1} to 1627 cm^{-1} and the $\nu\text{ N-H}$ bond from 3250 to 3330 cm^{-1} . The X-ray diffractogram shows three additional small peaks at $2\theta = 7.6, 15.4$ and 17.2 , whose intensities increase with increasing amount of encapsulated TCG. As the SEM micrographs show no changes after encapsulation, we believe that the additional peaks are due to distortion of the cubic structure of Wessalith® by the host. Encapsulation of TCG was proven by pyrolysis coupled to mass spectrometry (Shimadzu Direct Sample Inlet Device - DI-50, Shimadzu Mass Detector - QP-5000). While TCG precipitated on Wessalith® at 60°C gives a mass spectrum similar to that of free TCG, encapsulated TCG gives only a minor peak (< 5%) for cyclohexylamine at 60°C . Encapsulated TCG decomposes at 150°C giving a mass spectrum equivalent to that reported for hexamethylene-1,6-diisocyanate (NIST62 library, SI of 90%). This result clearly shows that the TCG is not impregnated onto the external surface of Wessalith® and can only leave the supercage after decomposition into smaller molecules.

In order to test the catalytic activity we chose the condensation reaction of acetone with benzaldehyde to form 4-phenyl-3-buten-2-one. Alkali and alkaline earth metal hydroxides in dilute solution are highly effective catalysts for this reaction.¹¹ In the presence of 10 mol % of TCG, benzaldehyde can be quantitatively condensed with acetone at r.t. giving, after 7 h, 4-phenyl-3-buten-2-one with 90% selectivity.¹² Encapsulated TCG (10 mol %) in Wessalith® produces 4-phenyl-4-hydroxybutan-2-one (86% selectivity) as the principal

product as well as some 4-phenyl-3-buten-2-one (14% selectivity), which is opposed to the reaction in homogeneous phase or to TCG precipitated on Wessalith[®], which gives the condensation product alone. The conversion, however, is lowered to 56% after 6 d. If the TCG encapsulated in Wessalith[®] is not neutralized with lithium carbonate, the conversion is further reduced (15% in 15 d) and 4-phenyl-3-buten-2-one is again the main product. Neither Wessalith[®] nor lithium carbonate alone or its combination show any catalytic activity. Further investigation is necessary to explain the loss of activity of the encapsulated TCG. Tentative explanations are that the encapsulated TCG is less basic due to a lower symmetry of the guanidinium cation, or less reactive due to a lower rate of proton transfer in the supercage.¹³ In continuation of this study we will prepare other guanidines encapsulated in Wessalith[®] in order to understand the reason for the reduced activity and the different selectivity.

Acknowledgments: This work was supported by grants from Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) and Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq). The authors acknowledge fellowships from FAPESP and CNPq and thank Drs. Regina Buffon, Martin Wallau, Fernando Luna and Antonio Pedro de Oliveira Filho for helpful discussions.

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8. Wessalith[®] DAY was kindly provided by Degussa AG, Germany. It has the FAU structure (7.4 Å channels and 13 Å supercages), Si/Al ratio > 100, a BET surface area of 700 m²/g and was dried at 100°C for 24 h.
9. Wessalith[®] (1.0 g) was suspended in a solution of 0.144 g (0.70 mmol) of *N,N'*-dicyclohexylcarbodiimide (DCC) in 2.2 mL of *tert*-butanol at r.t. for 24 h. Cyclohexylamine (0.145 g, 1.46 mmol) was added and the mixture refluxed for 24 h. After the reaction, another 5.0 mL of *tert*-butanol were added and the reaction mixture filtered. The solid was neutralized with a suspension of lithium carbonate in dry methanol at r.t. for 2 h. It was then washed with 20 mL of chloroform and dried at 50°C under reduced

pressure. Microanalysis gave 9.63% C, 1.47% H and 1.76% N, which correspond to 0.42 mmol of TCG encapsulated in 1.0 g of Wessalith®.

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12. In a 10 mL flask 0.35 g (3.3 mmol) of benzaldehyde in 0.7 mL of methanol were reacted at r.t. with 0.56 g (9.7 mmol) of acetone in the presence of 0.098 g (0.32 mmol) of TCG or 0.85 g (0.34 mmol) of encapsulated TCG in Wessalith®. The reaction products were quantified by GC analysis, using a 25 m×0.22 mm×0.33 µm CBP1 column, a FID detector and cyclooctane as internal standard.
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(Received in USA 4 December 1996; accepted 6 January 1997)