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Nanoporous solids as receptacles and catalysts for unusual conversions of organic compounds

Robert Raja [a,*], John Meurig Thomas [b,c,*]

[a] *Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK*
[b] *Davy Faraday Research Laboratory, The Royal Institution of Great Britain, 21 Albemarle Street, London W1S 4BS, UK*
[c] *Department of Materials Science & Metallurgy, University of Cambridge, Pembroke Street, Cambridge CB2 3QZ, UK*

Abstract

Solid-state chemical principles, allied to a degree of chemical intuition, enables one to design open-structure solids on to the inner surfaces of which isolated catalytically active sites of different kinds may be placed. With such solids, which act simultaneously both as permeable catalysts and reaction vessels, a number of highly desirable chemical conversions—many of paramount importance in the context of "green" chemistry and clean technology—may be smoothly effected under environmentally benign conditions. Typical examples, illustrated here, include the selective oxidation of toluene to benzaldehyde, current methods of producing alcohols, aldehydes and acids, and the synthesis of ε-caprolactam in a by-product-free manner. Such open-structure solids, which house single-site active centres, are also readily amenable to detailed and precise structural elucidation.

Keywords: Single-site heterogeneous catalysts; "Green" chemistry; Oxidation of alcohols; Nylon-6; Polymer recycling; Microporous aluminophosphates

1. Introduction

Oxidation processes account for a large fraction of the chemicals that are manufactured from petroleum and its products; and traditionally the methods used for doing so have relied heavily on the use of stoichiometric reagents—substances like CrO_3, $Na_2Cr_2O_7$, CrO_2Cl_2, $KMnO_4$, etc., that donate oxygen atoms to be incorporated into the desired material. Interestingly, all the above reagents are enumerated as the ones of choice in recent textbooks [1,2] of organic chemistry dealing with the oxidation of alcohols to aldehydes or acids. In an age when it is necessary, for ecological and other reasons, to use benign reagents like H_2O_2, or better still O_2 or air, as the oxidant, it also becomes necessary to design suitable solid catalysts that can enable oxidations to occur under mild conditions, and in such a way as to enable the products readily to be separated from unconverted reactants.

We have shown elsewhere how to design a microporous solid—an Fe^{III}-substituted aluminophosphate [3], or an oxo-centred tricobalt complex [4] anchored on the inner walls of a mesoporous silica—so as to be able to oxidize cyclohexane to adipic acid [3] or to mixtures of cyclohexanone and cyclohexanol [4]. Here we address the challenging task of converting cyclohexanone (**1**), in a benign fashion, to ε-caprolactam (**2**), the precursor of nylon-6. Nylon-6 is currently used for a wide variety of purposes: in the textile industry (lingerie, hosiery, sportswear, leisurewear, fashion wear, linings, parachutes, umbrellas, tents and sleeping bags), floor coverings (carpets and rugs), industrial yarns (tyres, conveyor belts, ropes, nets, fishing lines and tarpaulins), engineering plastics (automotive air-inlets, engine covers and aircraft windows) and in films (food and industrial packaging). It is the polymerised product of ε-caprolactam, which is currently manufactured in two distinct ways, each being a two-step process involving extremely aggressive reagents (Scheme 1). Moreover, these two ways of manufacture generate four times the mass of ε-caprolactam as ammonium sulfate, a costly waste product to render neutral or useful.

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[*] Corresponding author. Fax: +44 1223 336017 (R. Raja), fax: +44 1223 740360 (J.M. Thomas).

E-mail addresses: rr243@cam.ac.uk (R. Raja), jmt2@cam.ac.uk (J.M. Thomas).

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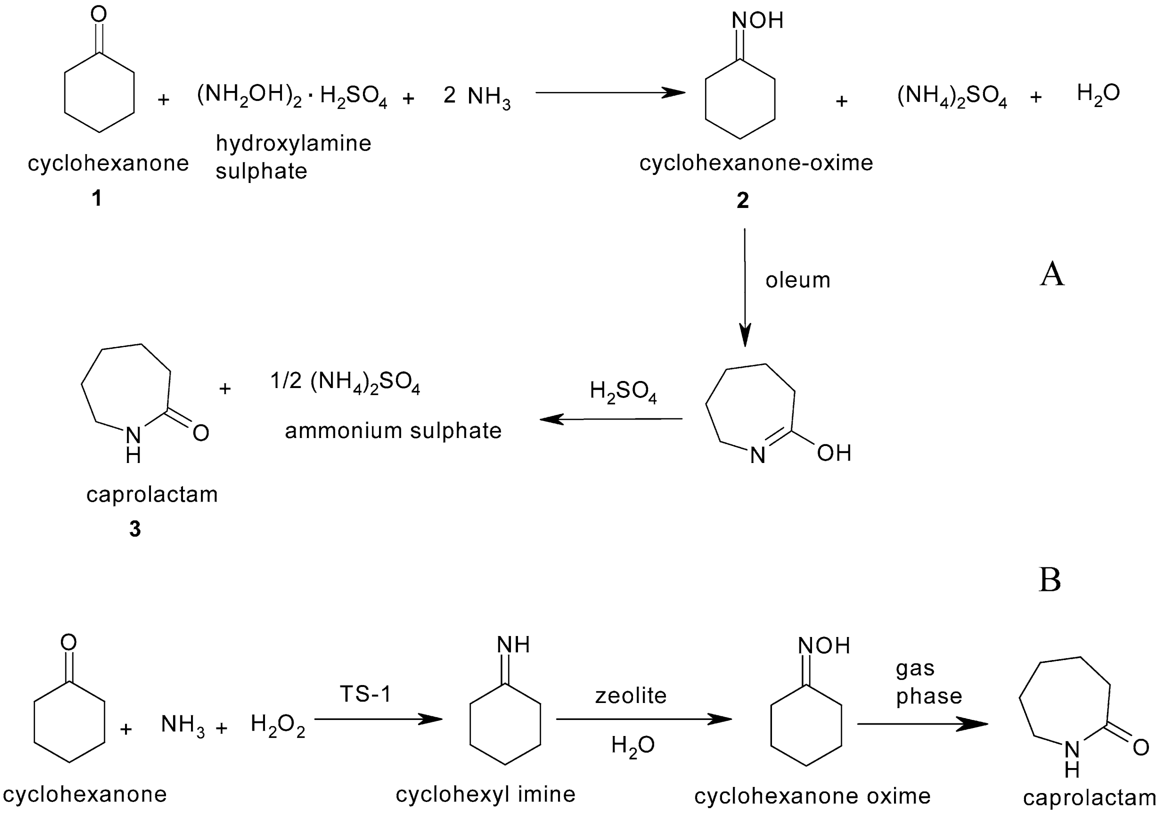

Scheme 1.

Our aim, when we embarked [5] on the task of devising a low-temperature, solvent-free benign method of synthesizing ε-caprolactam, was to identify a family of single-site catalysts, that could be controllably tuned to yield maximal efficiencies in regard to the production of (i) hydroxylamine (NH_2OH) under in situ conditions and (ii) ε-caprolactam.

Before we proceed to outline the key aspects of the solid-state chemical arguments—and some of the remaining problems associated with a viable route to ε-caprolactam—we first reflect on the (environmentally) unsatisfactory state of affairs that pertain to certain aspects of the current practice in producing (i) aldehydes or acids from hydrocarbons and (ii) alcohols or acids from aldehydes.

2. Current methods of producing aldehydes, alcohols and acids

Massive amounts of these products are used annually worldwide, in a large variety of chemical, pharmaceutical and agrochemical contexts. Take, for example, benzaldehyde. A leading text book of organic chemistry, one of the premier ones in the 20th century by Fieser and Fieser [6], had this to say about its manufacture:

> "The chief technical process for production of benzaldehyde, required as an intermediate for dyes and other synthetic chemicals and in flavors and soap perfumes, utilizes toluene as the starting material. One efficient method of conversion into the aldehyde is side-chain chlorination in Pyrex glass or porcelain reactors (preferably with illumination), fractionation, and hydrolysis of the benzal chloride cut. The hydrolysis is accompanied with water at 95–100° in the presence of iron powder or ferric benzoate as catalyst, lime is then added for neutralization and the benzaldehyde is steam distilled. Benzoic acid usually appears as a by-product."

$$C_6H_5CH_3 \longrightarrow C_6H_5CHCl_2 \xrightarrow[76\%]{} C_6H_5CHO$$

The same authors give details of another method of transforming toluene to benzaldehyde, using the classic Étard reaction:

> "A solution of two equivalents of chromyl chloride (CrO_2Cl_2) in carbon disulphide is added cautiously to the hydrocarbon with control of the temperature to 25–45°. The red colour of the reagent is discharged slowly and a chocolate-brown crystallizate separates consisting of a molecular complex containing two equivalents of the inorganic compound. The dry solid on treatment with water decomposes to give the aldehyde and an aqueous solution containing chromic acid and chromic chloride, and the aldehyde must be removed rapidly by distillation or solvent extraction to avoid destruction".

$$ArCH_3 + 2CrO_2Cl_2 \longrightarrow ArCH_3{\cdot}(CrO_2Cl_2)_2 \xrightarrow{H_2O} ArCHO$$

More recent text books of organic chemistry, for example, Clayden, Greeves, Warren and Wothers [2] give numerous examples of the oxidation. Two in particular are noteworthy. The first uses pyridinium dichromate (PDC), the second tetrapropylammonium perruthenate (TPAP) (see Scheme 2). Most of the