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Comparative Baeyer-Villiger oxidation of cyclohexanone on Fe-pillared clays and iron tetrasulfophthalocyanine covalently supported on silica

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ABSTRACT

The Baeyer-Villiger oxidation of cyclohexanone to caprolactone has been investigated at room temperature over AlFe-pillared clays, using oxygen as oxidant in the presence of benzaldehyde. A nearly complete conversion is observed with a selectivity into caprolactone above 80%. The observation of an induction period in the kinetics, of high activity of the non-pillared clay, and the detection of Fe traces in the reaction medium, suggest a process involving homogenous catalysis. The reaction is indeed catalysed in homogeneous phase by a few ppm of Fe. By contrast, iron phthalocyanine covalently supported on silica appears as a true heterogeneous catalyst, giving a selectivity above 95% to caprolactone at 61% conversion.

1. Introduction

The Baeyer-Villiger oxidation of ketones is a reaction of major synthetic interest in organic chemistry with a large range of possible applications spanning such diverse areas as the synthesis of antibiotics and steroids, the synthesis of pheromones for agrochemistry, the synthesis of monomers for polymerization. These reactions have been commonly carried out using peracids, such as persulfuric acid, perbenzoic acid, *m*-chloroperbenzoic acid (*m*-CPBA) and hydrogen peroxide (H_2O_2) [1–3]. Homogeneous catalysts have been proposed for various types Baeyer-Villiger reactions [4–8] allowing to reach regio- or enantioselective oxidations [9–12]. Heterogeneous catalysis has several advantages over homogeneous catalysis:

- simplicity in synthetic operations;
- prevention of the production of salt wastes during neutralization of the catalysts or reagents;
- reusability of the solid catalyst. Solid acids [13], polymer-anchored Pt complexes [14] or Bi(III) triflate [15] have been used as catalysts with aqueous H_2O_2 solution.

Corma et al. [16–21] reported that Sn/zeolite-beta was very active and selective for the Baeyer-Villiger oxidation of cycloketones or aromatic aldehydes with H_2O_2, leading to the synthesis of fragrance compounds. Natural clay minerals are eco-friendly and have been frequently used as catalyst support. Both palygorskite, $(Mg,Al)_5Si_8O_{20}(OH)_2(H_2O)_4{\cdot}4H_2O$ [22] and MgAl hydrotalcite exchanged by Sn [23] have been reported to catalyze the oxidation of cyclic ketones with H_2O_2.

Strategies consisting in the preparation of a peracid "in situ" have also been described: one approach uses nitriles as solvents and H_2O_2 in the presence of solid bases [24,25], leading to the intermediate formation of an iminoperacid. In this case the nitrile is a reactant, which is consumed in

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the reaction with formation of an amide. Murahashi et al. reported on this reaction forming a peracid in situ by reaction of benzaldehyde and oxygen for the first time [26]. This proposal was later extended by Kaneda et al. using a combination of molecular oxygen and aldehydes over Fe containing catalysts [27–34]. This process has been extended to various redox systems supported by cation exchangers [35], MCM-41 [36], modified silica [37] or zeolites [38] using O_2/PhCHO at low reaction temperatures. The catalyst was reusable without any appreciable loss in its activity and selectivity.

The use of Fe catalysts is attractive because the iron-containing compounds are considered to be of lower toxicity and are easily available. In this process, benzaldehyde can be converted to perbenzoic acid, which performs at room temperature, the reactions reported in Scheme 1. Fe-MCM has recently been reported to catalyse this reaction [36]. We report herein the Baeyer-Villiger oxidation of cyclohexanone by O_2-PhCHO in the presence of Fe-pillared clays and iron tetrasulfophthalocyanine covalently supported onto silica (FePcS-SiO_2).

2. Experimental

2.1. Preparation of the catalyst

The starting clay used was a montmorillonite from Maghnia, with a (001) spacing of 1.26 nm. The natural clay was purified by sedimentation in order to obtain small particles (< 2 μm) of pure montmorillonite (so-called Lalithe) [39]. The pillaring solution was prepared by slowly adding a measured amount of a 0.1 M $FeCl_3.6H_2O$ (97%, Aldrich) solution to a 0.1 M solution of chlorhydrol $Al_2(OH)_5Cl,2H_2O$, then aging this mixture during 18 h at room temperature. This solution was then added under stirring, to a 1 wt % suspension of the colloidal clay in water, then heated at 353 K, and maintained under stirring for 2 h at this temperature. The flocculating clay was then washed with distilled water until chloride free. The pillared clay was then dried and calcined 5 h to 623 K, reached with a temperature ramp of 5 K/min. The two solids used here were prepared with a ratio Al/clay = 10 mmol/g for the Al-pillared clays, and 10 mmol Al^{3+} mmol Fe per g for the AlFe-pillared clays (Table 1). They show after intercalation an interlayer spacing of about 2 nm, reduced to 1.7 nm after calcinations above 300 °C. The surface areas of the calcined materials are reported in Table 2. Both types of compounds show a surface area above 210 m^2/g, and similar size of pores.

Table 1
Chemical compositions and basal d_{001} spacings of the clays used as catalysts.

Sample	% SiO_2	% Al_2O_3	% Fe_2O_3	d_{001}
Original clay	67.18	20.49	2.39	1.25
$Al_{10}Fe_0$	54	38	2	1.95
$Al_{10}Fe_3$	51	28	17	2.14

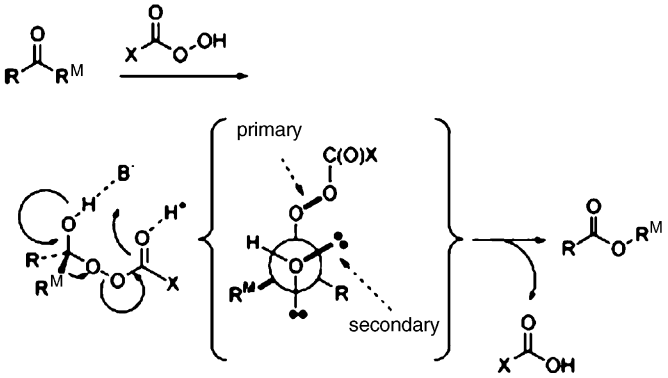
Table 2
Specific surface areas and porosities of the pillared clays.

Sample	$Al_{10}Fe_0$	$Al_{10}Fe_3$	Original clay
S_{BET} (m^2/g)	209	261	10
$S_{\mu p}$ (m^2/g)	152	144	/
$V_{\mu p}$ (mL/g)	0.075	0.074	/
Pores diameter (nm)	2.48	2.43	9.60

The heterogeneous catalyst FePCS-SiO_2 was prepared according to published procedure [40]. A solution of 52 mg of $FePc(SO_2Cl)_4$ in 20 mL of pyridine was stirred for 18 h. Then this solution was added to a suspension of 1.5 g of amino-modified amorphous silica (0.5 mmol of NH_2 per 1 g, prepared from Degussa Aerosil 200 and 3-aminopropyltriethoxysilane) in 12 mL of pyridine at 20 °C under Ar. The resulting mixture was stirred at 20 °C for 1.5 h, then at 80 °C for 24 h. A green material was separated by filtration and washed with acetone and water. The material was dried under vacuum at 80 °C for 24 h and characterized by chemical analysis, surface area determination (185 m^2/g) and the diffuse reflectance UV-vis spectroscopy that evidenced the effective complex grafting (360, 436 and 682 nm). The complex loading was determined by metal analysis using an inductively coupled plasma-mass spectrometry method to be equal to 26.9 μmol/g. The covalent linkage is provided by a sulfamide bonds between amino-groups of silica surface and sulfochloride functions of FePcS.

2.2. Catalytic reaction

The catalytic reaction was the Baeyer-Villiger oxidation of cyclohexanone using benzaldehyde and oxygen at room



Scheme 1. Mechanism of Baeyer-Villiger oxidation of aldehydes and ketones.