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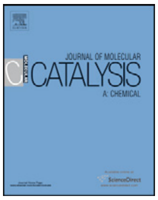

K-10 montmorillonite: An efficient and reusable catalyst for the aerobic C—C bond cleavage of α-substituted ketones

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ABSTRACT

A commercially available acid-activated montmorillonite clay catalyst, K10 montmorillonite, was tested for the catalytic oxidation of cyclic ketones in the presence of molecular oxygen under mild conditions (343 K and atmospheric pressure). K10 montmorillonite catalyzed the oxidative cleavage of C—C bonds in 2-methylcyclohexanone, 2-phenylcyclohexanone, 2-hydroxylcyclohexanone and 1,2-cyclohexanedione with good activity and excellent selectivity toward the formation of the corresponding ketoacids and diacids. The effects of acidity, amount of catalyst, temperature and solvent on the catalytic activity were investigated. Furthermore, this catalyst was reusable without any appreciable loss in activity and selectivity.

1. Introduction

The oxidative cleavage of cyclic ketones and their substituted derivatives is the main pathway for the synthesis of diacids and ketoacids on both the laboratory and industrial scales [1]. Due to ever-growing environmental concerns, there is a strong need for the establishment of promising catalytic protocols using molecular oxygen as an oxidizing non-toxic agent [2]. For that reason, many transition metal-catalyzed aerobic processes, both homogeneous and heterogeneous, have been developed.

The conversion of cyclohexanone or of cyclohexanol–cyclohexanone mixtures (KA oil) to adipic acid, one of the starting materials of Nylon® 6-6, is the most important application of this reaction [3]. Nitric acid is used as the oxidant in current processes, thereby leading to pollution with the formation of side-products such as NO_x and N_2O [4]. Similarly, laboratory-scale experiments based on stoichiometric oxidants like $Pb(OAc)_4$, $NaIO_4$, *etc.* [1,5] result in the formation of large amounts of solid toxic wastes which are not easily recyclable. The use of such oxidants have also some drawbacks that include corrosion, loss of catalyst, environmental issues and formation of unwanted side products along with the desired one reducing the yield of the latter. Efforts have therefore been made to develop homogeneous catalysts [6] and eco-friendly heterogeneous catalysts for the synthesis of industrially important ketoacids. In this context, we have demonstrated that Nafion® supported vanadium oxo species [7] catalyze efficiently the aerobic cleavage of C—C bonds in some α-ketols with good yields and can be recycled.

The clay catalysts and montmorillonite in particular, have received considerable attention for different organic syntheses because of their environmental harmlessness, low cost, high selectivity, reusability and operational simplicity [8]. The reactions catalyzed by montmorillonite are generally carried out under mild conditions, the separation of the spent catalyst is achieved by filtration, and the product is recovered by mere evaporation of the solvent. Furthermore, the montmorillonite catalysts can be regenerated easily and reused [9].

Montmorillonite is classified as a 2:1 clay, which means that one octahedral sheet is sandwiched between two silica tetrahedral sheets, and belongs to a highly disordered group of smectites [10]. Water molecules are readily absorbed by montmorillonite, forming hydration shells around the interlayer cations rather than continuous sheets [11]. The cation exchange capacity (CEC) is defined as the maximum amount of any one cation that can be taken up by a given clay [10]. Montmorillonite, as smectites in general, has a high cation exchange capacity, which ranges from 70 to 130 mequiv. per 100 g [12]. Most of the exchange capacity (80%) is due to

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substitution within the structure, but a smaller amount (20%) is due to the charges at the edges of the sheets [13].

Acid-activated clays are efficient and relatively inexpensive solid acid catalysts for liquid phase processes [14]. There is, therefore, a great variety in the type and activity of acid treated clays. Despite the discovery of many new inorganic mesoporous molecular sieves on which solid acids can be based, activated clays remain one of the most important and widely used classes of mesoporous solid acid catalyst available in industry [15].

One commercial example is K-10 montmorillonite, which is obtained from the natural montmorillonite by treatment with mineral acids at 96–98 °C. The natural montmorillonite structure is progressively destroyed, resulting in a loss of crystallinity but a significant increase in surface area and acidity in comparison to the natural clay [16]. K-10 montmorillonite clay has been widely used as catalyst in a large variety of organic reactions [17–21] and it has also received considerable attention in different areas of organic synthesis [22–27].

In the present study, we report the aerobic cleavage of C—C bonds in α-substituted ketones catalyzed by K-10 montmorillonite (referred to as K-10MT). Most experimental parameters such as the addition of organic and inorganic acids, amount of catalyst, temperature and solvent nature were systematically studied. The results are compared to those obtained with a synthetic transition-metal free montmorillonite.

2. Experimental

2.1. Chemicals

Aerosil silica (Degussa), magnesium acetate (Prolabo, 98%), boehmite alumina (Sassol, Pural SB-1), sodium acetate (Pro-analysi, ≥99%), acetic acid (Riedel de Haën, ≥99%), acetonitrile (Riedel de Haën, ≥99.5%), methanol (Riedel de Haën, ≥99.8%), sulfuric acid (Solvachim, 98%), fluorhydric acid (VWR, 40%), heptanoic acid (Aldrich, ≥97%), 2-methylcyclohexanone (Aldrich, 99%), 2-phenylcyclohexanone (Aldrich, 99%), 2-hydroxycyclohexanone (Aldrich, 99%), 1,2-cyclohexanedione (Acros, 98%) were used as received without any further purification.

The K-10 montmorillonite (K-10MT) used in this work was purchased from Aldrich with a surface area (S_{BET}) of 269 $m^2\,g^{-1}$. The composition (wt.%) of K-10MT determined by X-ray fluorescence (XRF) was: 82.67% SiO_2, 13.93% Al_2O_3, 1.61% Fe_2O_3, 0.32% TiO_2, 0.10% CaO and 1.36% K_2O. The calculated cation exchange capacity was 0.8 mequiv./g clay.

2.2. Preparation of synthetic montmorillonite

In order to evaluate the possible activity of a transition-metal free montmorillonite, a Mg containing synthetic clay, denoted S-MMT, was prepared according to a procedure previously reported by Reinholdt et al. [28]. Briefly, a transition-metal free sample was synthesized in an acidic fluoride medium (caution should be taken when using HF which can cause severe burns to tissue and is lethal) using a Teflon-lined stainless steel autoclave under hydrothermal conditions with the following molar gel composition:

$$1SiO_2{:}0.2Al_2O_3{:}0.1MgO{:}0.05Na_2O{:}0.05HF{:}96H_2O$$

After 72 h reaction time at 493 K, the autoclave was allowed to cool and the white precipitate was filtered. The pH of the filtrate was 4.2. The solid was thoroughly washed using Milli-Q® water and finally dried at 333 K for 12 h.

2.3. Characterization techniques

X-ray diffraction patterns were obtained with a Panalytical X'Pert Pro diffractometer equipped with a X'Celerator detector using Fe-filtered Co-Kα radiation. The data were collected at room temperature with a 0.017° step size in 2θ (scan step time = 25 s), from $2\theta = 5$ to 110°. The crystalline phase was identified by comparison with ICSD reference files.

X-ray fluorescence analyses were carried out using a Panalytical Minipal 4 spectrometer equipped with a rhodium anode X-ray tube. The classical preparation method, with approximately 5 g of the solid, was not used. An original method based on the analysis of thin layers [29] and adapted to the geometry of the spectrometer (the analytical area of the Minipal 4 is exactly centered on the sample holder and corresponds to a diameter of 8 mm) was developed. Briefly, the intensity was first calibrated by depositing 15 μL of a known solution (1 g/L) of iron or calcium salt on polycarbonate thin membranes (uncertainties less than 1%). For the other elements, a deposit of a very small quantity of a geological powder material (CMR GH-CRPG) was deposited on a second polycarbonate film from a suspension in cyclohexane. For this standard material, the concentrations of all the elements under study are very well known and allow, comparatively to the response for pure iron or calcium deposits, to determine the sensitivity of other elements such as potassium, silicon, aluminum or magnesium. The sensitivity for all elements of interest is thus obtained. A few hundred of micrograms of the montmorillonite sample was deposited exactly in the same manner as for the geological material. Owing to the principle of thin layer analysis, the intensity is directly proportional to the mass of the analyzed element in the analytical area and allows to quantitatively analyze all the deposited powder. We consequently obtain the elemental mass of all the elements of interest in the montmorillonite sample.

SEM-FEG images were obtained using a Zeiss SUPRA 40 FESEM that is completely controlled from a computer workstation. The electron source is a thermal field emission gun (Schottky type). Images are created using the SMARTSEM software. Prior to analysis, the samples were coated with a 5 nm carbon layer using a Cressington 208 carbon high vacuum carbon coater.

TEM experiments were performed using a Jeol JEM 100CXII transmission electron microscope operating at 100 kV. One drop of an ethanolic suspension of the as-produced particles was deposited on the carbon membrane of the microscope grid for the observations.

Adsorption and desorption nitrogen isotherms were obtained at 77 K using a Micromeritics ASAP 2020 apparatus. The samples were outgassed at 423 K and 0.1 Pa for 12 h before measurements. Specific surface area (S_{BET}) values were obtained using the Brunauer–Emmett–Teller equation with relative pressures in the range 0.05–0.20.

NH_3 chemisorption experiments were realized with a Belsorp apparatus. Samples were first outgassed at 423 K and 10 Pa for 12 h before measurements. The total number of acid sites (Lewis and Brönsted) was determined using the following method. A first isotherm corresponding to physically and chemically adsorbed ammonia was obtained at 373 K. Then outgassing at 423 K for 3 h was performed and a second ammonia adsorption experiment performed at 373 K gave a second isotherm. This second isotherm corresponds to physically only adsorbed ammonia. The difference between the first and the second isotherm is the total chemisorbed amount (the total acidity).

2.4. Catalytic tests

All catalytic tests were carried out using Schlenk techniques (20 mL) which was attached to a vacuum line with a manometer