Journal of Molecular Catalysis A: Chemical 363–364 (2012) 437–445

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

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

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ARTICLE INFO

Article history:
Received 9 May 2012
Received in revised form 16 July 2012
Accepted 18 July 2012
Available online 8 August 2012

Keywords:
K-10 montmorillonite
Dioxygen
α-Substituted ketones
Oxidative cleavage

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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http://dx.doi.org/10.1016/j.molcata.2012.07.022

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 2θ = 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

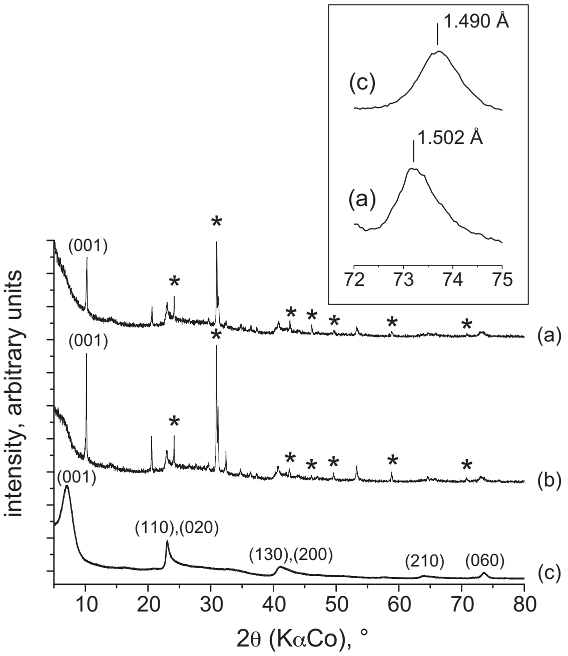


Fig. 1. X-ray diffraction patterns for: (a) uncalcined K-10MT, (b) K-10MT after catalysis test (corresponding to Table 2, entry 3) and (c) synthetic montmorillonite S-MMT: ⋆: quartz (JCPDS no. 01-078-1252). Inset: enlargement of the (0 6 0) reflection.

and a gas inlet. Prior to each catalytic test, the clay was dried at 373 K for 2 h. In a typical experiment, the Schlenk was charged with the solvent (5.0 mL; solvent: CH_3CN, H_2O, CH_3OH, CH_3COOH or a mixture of CH_3COOH and H_2O) and K-10MT (0.20 g). In some tests H_2SO_4 (0–0.37 mmol) was also added. The substrate (5.0 mmol) was then added and the vessel was immersed in an oil bath preheated at 70 °C. O_2 was introduced at atmospheric pressure and the mixture was stirred magnetically for 24 h. Three parallel catalytic experiments were carried out for each test.

Dioxygen uptake was determined using a thermostated (70 °C) gas burette system connected to the reactor. The addition of heptanoic acid as an internal standard at the beginning of the experiment permitted to quantitatively analyze the products using a Shimadzu GC-17A gas chromatograph equipped with a TRA-5 column (30 m × 0.25 mm internal diameter) and a flame ionization detector. GC conditions: initial temperature, 80 °C for 10 min; ramp rate, 10 °C min^{-1}; final temperature, 220 °C; injection temperature, 220 °C; detector temperature, 250 °C; carrier gas, He at 25 mL min^{-1}. Absolute errors were estimated to be about 5%.

After catalysis test, the catalyst was recovered following the recommendations proposed by Sheldon [30]: the solid was filtered at the reaction temperature, *i.e.* 70 °C, washed three times with distilled water and dried at 373 K for 12 h. The powders were characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The recovered catalyst was also used for recycling experiments.

3. Results and discussion

3.1. Characterization of the materials

3.1.1. Structural and morphological studies

The X-ray diffraction patterns of the K-10MT and synthetic montmorillonites are presented in Fig. 1a and c, respectively. They exhibit characteristic reflections usually observed for smectites [28,31]. The basal spacing (d_{001}) for K-10MT and the synthetic montmorillonite are 10.3 and 14.5 Å, respectively. The d_{001} interreticular distance of a synthetic material natural montmorillonite under a relative humidity of 80% has been reported by Reinholdt et al. to be about 15 Å [28]. Because of the swelling properties of smectites, the position of the (0 0 1) reflexion depends on the water content of the material which in turn depends on the relative humidity of the atmosphere in which the materials have been stored. The different (0 0 1) positions observed for K-10MT and S-MMT could thus be explained by different water amounts in the interlamellar space of the clay mineral. The basal spacing d_{001} of montmorillonite K-10MT "with K as predominant exchangeable cations" is 10.3 Å in agreement with zero-layer hydration state. The synthetic montmorillonite under high humidity conditions and in presence of Na^+ exchangeable cation shows the increase in the basal spacing corresponding to the two layers hydration state (d_{001} = 14.5 Å). Moreover, the (0 0 1) peak is clearly broader for S-MMT than for K-10MT which can be explained considering: (i) a higher crystallization state for K-10MT than for S-MMT and/or (ii) smaller crystallite sizes for S-MMT (this latter point is in agreement with the SEM-FEG observations, *vide infra*). The two samples exhibit a peak at about 73° attributed to the (0 6 0) reflection of dioctahedral phyllosilicates [28]. It is well known that for dioctahedral smectites, *i.e.* containing vacancies in the octahedral layer, the (0 6 0) reflection is expected at 1.49 Å, whereas for trioctahedral materials, this reflection is at 1.52 Å [28,31]. For S-MMT d_{060} is 1.49 Å whereas for K-10MT, it is 1.50 Å. Both values are indicative of dioctahedral smectites. Note that for K-10MT, peaks corresponding to quartz (JCPDS no. 01-078-1252) are also unambiguously identified; this has already been observed by other authors [31,32].

The SEM-FEG micrographs of samples K-10MT and S-MMT are presented in Fig. 2a and b, respectively. They show clearly the lamellar nature of the materials. The S-MMT clay exhibits a more divided state than K-10MT and is made of crumpled platelets as reported previously by Reinholdt et al. [28].

The TEM image displayed in Fig. 2c shows also the lamellar nature of the K-10MT montmorillonite. The d_{001} value, determined with the numerical electron diffraction pattern, is found to be 10.1 Å and is in excellent agreement with the value determined by X-ray diffraction.

The clays were also characterized using physisorption techniques. Both materials exhibit type II isotherms according to the IUPAC classification [33] with a H3 hysteresis type, usually obtained for aggregates of platy particles or adsorbents containing slit-shaped pores (Fig. S1, Supplementary materials). The C BET constants found for K-10MT and S-MMT are 111 and 264, respectively. The significant higher C BET value for S-MMT than for K-10MT can indicate the existence of microporosity for the former. The specific surface areas, determined using the BET method, are 269 and 132 $m^2\,g^{-1}$ for K-10MT and S-MMT, respectively. The important difference in the S_{BET} values can be explained taking into account that the commercial K-10MT sample has been activated by mineral acids which leads to a loss of crystallinity but a significant increase in surface area compared to the natural clay [16]. Conversely, even if S-MMT has been prepared in a highly acidic fluoride medium, it has not undergone a post-treatment which can alter its textural properties.

3.1.2. Ammonia chemisorption

Ammonia chemisorption has been carried out at 373 K in order to evaluate the acidic properties of the two samples. The obtained isotherms are presented in Fig. 3 and the number of total (Lewis and Brønsted) acid sites is given for the two samples in Table 1. The values (expressed in mmol g^{-1}) obtained here are close to that reported by Flessner et al. for similar solids [34]. However, when normalized to the specific surface area value, S-MMT displays a

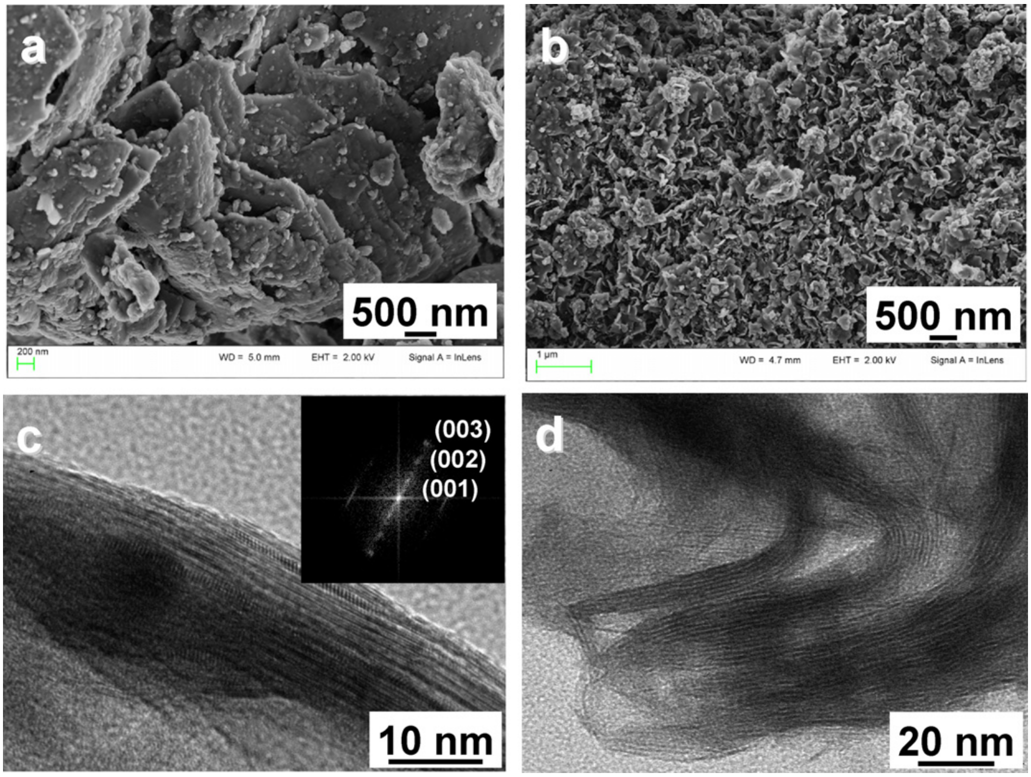


Fig. 2. SEM-FEG images of (a) dried K-10MT and (b) S-MMT and TEM images of (c) dried K-10MT (inset: numerical electron diffraction pattern) and (d) K-10MT after catalysis test (corresponding to Table 2, entry 3).

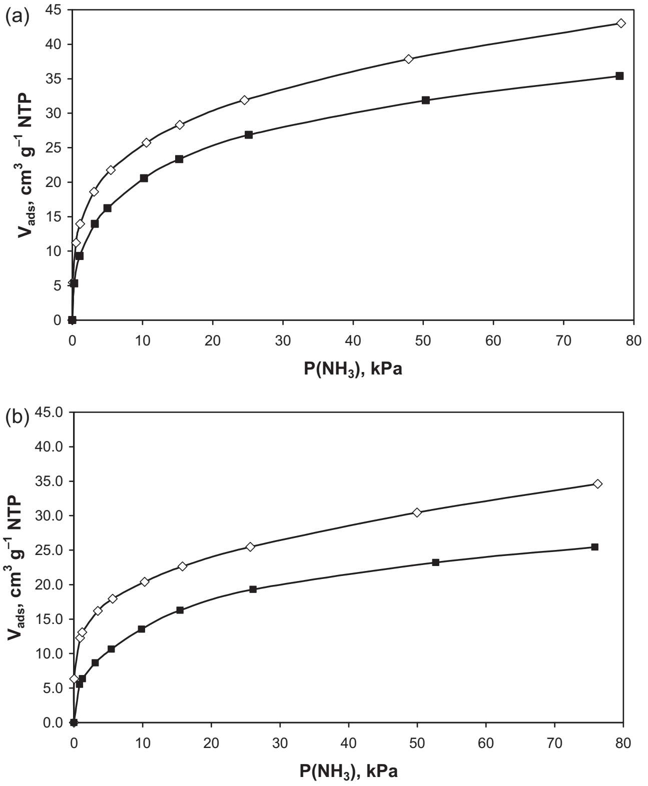


Fig. 3. NH_3 chemisorption isotherms at 373 K for (a) K-10MT and (b) S-MMT: ◇, first isotherm; ■, second isotherm.

higher number of acid sites per unit surface area than K-10MT. This result could be explained considering that: (i) S-MMT has been synthesized in a highly acidic fluoride medium and (ii) protons can readily exchange with other cations present in the inter-lamellar space.

3.2. Reactivity

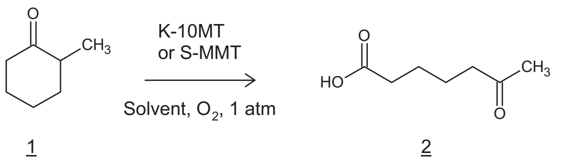
3.2.1. Oxidation of 2-methylcyclohexanone

We have first studied the oxidative cleavage of carbon—carbon bonds in α-substituted ketones using commercial K-10MT and synthetic montmorillonite S-MMT as heterogeneous catalysts and dioxygen as a clean oxidant. While K-10MT contains iron and titanium cationic species, S-MMT is transition-metal free (see Sections 2.1 and 2.2). Initially, the oxidation of 2-methylcyclohexanone, **1**, to 6-oxoheptanoic acid, **2**, was chosen in order to investigate the catalytic activity, selectivity, and stability of the clays (Scheme 1). Note that test experiments realized under the same conditions, but in the absence of a catalyst, showed that the ketoacid cannot be obtained.

The catalytic results obtained with the two sets of catalysts, K-10MT and S-MMT are presented in Table 2. In methanol, the data clearly show that K-10MT is an efficient catalyst contrary to S-MMT, since no conversion is observed with the latter. Nevertheless, a moderate yield is obtained with K-10MT if no acid is added in the

Table 1
Specific surface areas and number of total acid sites determined by ammonia chemisorption at 373 K.

Sample	S_{BET}, $m^2\ g^{-1}$	Number of acid sites, mmol g^{-1}	Number of acid sites, μmol m^{-2}
K-10MT	269	0.23	0.85
S-MMT	132	0.34	2.57



Scheme 1. Heterogeneous oxidation of 2-methylcyclohexanone, with dioxygen and catalyzed by commercial K-10MT and synthetic montmorillonite S-MMT.

reaction medium indicating that the intrinsic acidity of the clay is not sufficient to induce appreciable conversion of the substrate. The improvement of the catalytic activity with the addition of acids is well known [6,7,35,36]. Several reasons have been proposed: (i) the oxidation reaction proceeds first *via* the formation of the enol tautomer from the cyclic ketone, which is enhanced in the presence of protons [6,7,35,36], (ii) peracetic acid could be generated *in situ* from acetic acid, the former acting as an oxidant [36] and (iii) the protonation of the cyclohexanone may facilitate its dissolution as far as water is used as the solvent [36] (the solubility of 2-methylcyclohexanone is about 2 g per 100 mL at 20 °C [37]). For instance, previous results obtained with the homogeneous system $Cu(NO_3)_2{\cdot}3H_2O/O_2/AcOH/H_2O$ at 60 °C have shown that the highest 2-methylcyclohexanone conversion and highest ketoacid yield were obtained for the $AcOH/H_2O = 4.5/0.5$ mL/mL composition [6]. Recently, Cavani et al. have also shown the dramatic influence of acetic acid used as a co-solvent for the oxidation of cyclohexanone into adipic acid in the presence of $H_{3+n}[PMo_{12-n}V_nO_{40}]{\cdot}aq$ ($n = 1$ and 2) polyoxometalates: the highest conversion was observed for an equivolumetric mixture of water and acetic acid [36]. Moreover it was shown that, in presence of acetic acid, besides the redox mechanism, a radical-chain auto-oxidation mechanism prevailed when a very low catalyst/cyclohexanone was used. For K-10MT, the use of a water/acetic acid mixed solvent also allowed to increase considerably the conversion and the yield toward the ketoacid (see Table 2, entry 2). The catalytic activity could be further increased adding a small amount of sulfuric acid (see Table 2, entry 3). The results displayed in Table 2 also show that the transition metal-free S-MMT is inactive toward the oxidation of 2-methylcyclohexanone, indicating that if acidity is needed, transition metal species are mandatory.

3.2.1.1. Effect of catalyst amount and effect of substrate amount. Fig. 4a shows the effect of the amount of K-10MT catalyst on the conversion of 2-methylcyclohexanone, using a mixed water/acetic acid (4.5/0.5 mL/mL) solvent in the presence of a small amount of H_2SO_4. The amount of K-10MT catalyst was increased from 0 to 0.7 g. In the absence of catalyst, the ketoacid could not be obtained. The conversion of the ketone increased with the amount of catalyst, reaching a maximum of 70% for 0.2 g. This point can be explained by the increase in the number of acid and redox sites available for oxidation reaction. Further increase in catalyst amount, beyond 0.2 g, resulted in a decrease of the conversion of the substrate. Cavani et al. have recently reported that in the presence of acetic acid, two overlapping reaction mechanisms can account for the product distributions: a redox mechanism (predominant in absence of acetic acid) and a radical auto-oxidation one (favored in the presence of acetic acid and low catalyst amounts) [36]. In our work, the decrease in ketone conversion could be explained by chain-termination effects as reported previously for Co-containing molecular sieves for the liquid phase oxidation of cyclohexane to adipic acid [38].

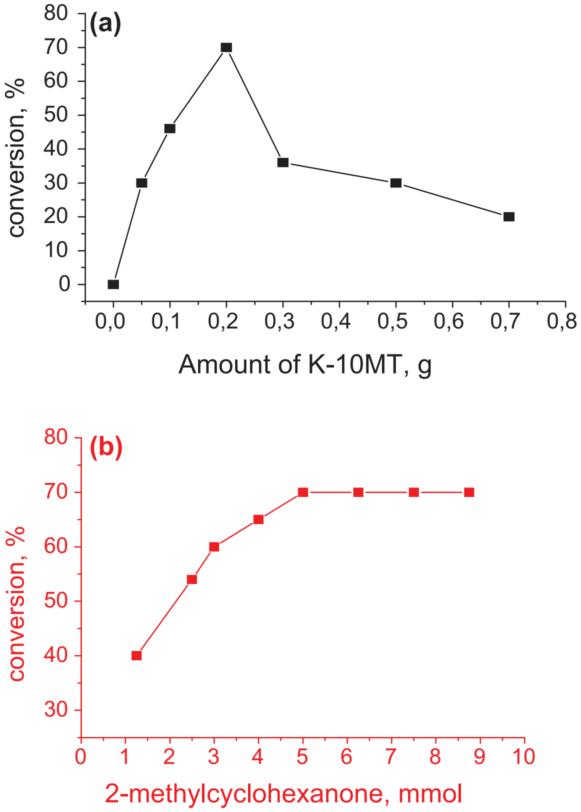


Fig. 4. (a) Effect of the catalyst mass on the conversion of 2-methylcyclohexanone. Conditions: substrate (5 mmol), $AcOH/H_2O$ (4.5 mL/0.5 mL), H_2SO_4 (0.37 mmol), $t = 24$ h, $T = 70$ °C, $P(O_2) = 0.1$ MPa and (b) effect of the 2-methylcyclohexanone amount with 0.2 g of catalyst at the same reaction conditions.

The effect of the initial amount of 2-methylcyclohexanone was investigated on the conversion in the range of 1.25–8.75 mmol, at 70 °C, by keeping the same amount of catalyst (0.2 g). As shown in Fig. 4b, the conversion increased with increase in quantity of 2-methylcyclohexanone reaching a maximum of 70% for 5 mmol. In the following, all the catalysis tests were thus performed using 0.2 g of solid montmorillonite and 5 mmol of substrate.

3.2.1.2. Effect of solvent. Preliminary studies with other catalytic systems have emphasized the important role of the solvent [6,39,40]. In this study, the effect of the solvent is also clear: after

Table 2
Oxidation of 2-methylcyclohexanone with K-10MT and S-MMT.

Entry	Catalyst	Solvent (mL)	mmol O_2	Conversion (%)	6-Oxoheptanoic acid yield (%)
1[a]	K-10MT	CH_3OH (5)	0.53	10	8
2		$AcOH/H_2O$ (4.5/0.5)	2.65	53	51
3[b]		$AcOH/H_2O$ (4.5/0.5)	3.50	70	68
4[a]	S-MMT	CH_3OH (5)	0	–	–
5		$AcOH/H_2O$ (4.5/0.5)	0	–	–
6[b]		$AcOH/H_2O$ (4.5/0.5)	0	–	–

Conditions: substrate (5 mmol, 0.6 mL), catalyst (0.2 g), $t = 24$ h, 70 °C, $p(O_2) = 0.1$ MPa.

[a] Reaction carried out at 60 °C.

[b] Test carried out with 0.37 mmol H_2SO_4.

Table 3
Effect of solvent on the oxidation reaction of 2-methylcyclohexanone.

Entry	Solvent (mL)	mmol O_2	Conversion (%)	6-Oxoheptanoic acid yield (%)
1	CH_3CN (5)	0.41	8	7
2[a]	CH_3OH (5)	2.50	50	48
3	H_2O (5)	1.10	22	19
4	$AcOH/H_2O$ (3/2)	1.60	32	30
5	$AcOH/H_2O$ (4/1)	2.97	59	57
6[b]	AcOH (5)	4.00	80	77
7	–	2.00	40	38

Conditions: substrate (5 mmol, 0.6 mL), K-10MT (0.2 g), H_2SO_4 (0.37 mmol), t = 24 h, 70 °C, $p\,(O_2)$ = 0.1 MPa.

[a] Reaction carried out at 60 °C.

[b] Reaction time 30 h.

24 h, the conversion reaches only 8% in acetonitrile whereas it is 22% in aqueous media (Table 3, entries 1 and 3). With pure methanol, higher values (50%) were obtained (Table 3, entry 2). It is difficult to explain the effect of solvent on the basis of their dipole moments or their dielectric constants, but, whatever the solvent used, excellent selectivities toward 6-oxoheptanoic acid were observed, between 86 and 97%. We believe that the solvent effect could be explained by the fact that the solubility of dioxygen differs from one solvent to another. Probably, when the mole fraction of dioxygen increase the catalytic activity increases.

Moreover, X-ray fluorescence analyses have shown that iron and titanium are present in K-10MT whereas the synthetic montmorillonite is transition metal free (*vide supra*). Thus, the active species could correspond to Fe(II) and/or Fe(III) species and/or Ti(IV). We think that the mixed solvent $AcOH/H_2O$ (4.5 mL/0.5 mL) facilitates the reduction rate of M^{n+} (M = Fe or Ti) and increases the solubility of dioxygen. By-products such as cyclopentanone are identified, but they are always produced in very low yield.

Note that without solvent, a moderate activity (38% yield) is observed but higher than with water (Table 3, entries 3 and 7). It is a very interesting result regarding environmental concerns because the exclusion of pollutants from an unselective preparation method is always preferable to subsequent treatment. In this context, the goal of modern organic synthesis is to develop efficient catalytic methods that can produce compounds with atom economy and environmental advantages.

With pure acetic acid (Table 3, entry 6) the conversion of 2-methylcyclohexanone can reach up to 80% but a longer reaction time is necessary (30 h). This is explained by an observed induction time (about 6 h) before reaction starts (see Fig. 5).

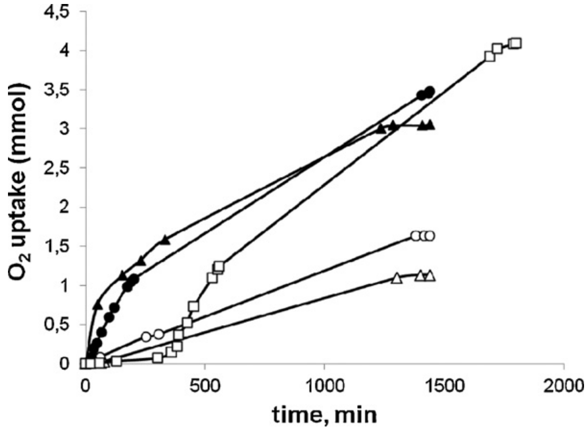


Fig. 5. O_2 consumption at 70 °C for different solvents using K10-MT for the catalytic oxidation of 2-methylcyclohexanone in (△) water, (□) AcOH and different $AcOH/H_2O$ mixtures: (○) 3 mL/2 mL; (▲) 4 mL/1 mL; (●) 4.5 mL/0.5 mL.

Table 4
Effect of temperature and acidity in the oxidation reaction of 2-methylcyclohexanone.

Entry	Temperature (°C)	mmol sulfuric acid	mmol O_2	Conversion (%)	6-Oxoheptanoic acid yield (%)
1	r.t.	0.37	0.52	10	8
2	40	0.37	1.35	27	26
3	70	–	2.65	53	51
4	70	0.18	3.00	60	58
5	70	0.37	3.50	70	68
6	70	0.55	3.50	70	68
7	70	0[a]	1.65	33	30
8	60	0[a,b]	0.60	12	10
9[c]	70	0[a,b]	–	12	10

Conditions: substrate (5 mmol, 0.6 mL), $AcOH/H_2O$ (4.5 mL/0.5 mL), K-10MT (0.2 g), t = 24 h, $p\,(O_2)$ = 0.1 MPa.

[a] Reaction carried out with a K-10MT sample (1.0 g) first treated with H_2SO_4 (1.85 mmol) in water (25 mL) for 5 h at 96 °C, recovered by filtration and dried at 100 °C for 12 h.

[b] Reaction carried out in methanol.

[c] In methanol under reflux conditions.

Based on previous studies [39,40] realized with homogeneous catalytic systems, mixtures of water and acetic acid were also evaluated. The best result (Table 2, entry 3) has been obtained for the $AcOH/H_2O$ = 4.5/0.5 v/v composition with a 68% yield for 6-oxoheptanoic acid after 24 h. Indeed, even if the initial rate is higher for the $AcOH/H_2O$ = 4/1 (v/v) composition than for the latter (see Fig. 5), the final conversion after 24 h is substantially lower.

In the following, the tests have been carried out with the $AcOH/H_2O$ = 4.5/0.5 (v/v) mixed solvent.

3.2.1.3. Effect of temperature and acidity. We have further studied the role of the temperature and the acidity on the conversion of compounds **1** to **2**. In this way, we realized the oxidation reaction at room temperature (Table 4, entry 1), at 40 °C (Table 4, entry 2) and at 70 °C (Table 4, entry 5). The yield in ketoacid was gradually increased from 8 to 68% after 24 h.

Moreover, previous work has shown the dramatic influence of the Brønsted acidity on the catalytic activity. For instance, the remarkable efficiency of HPA-*n*, *i.e.* $H_{3+n}[PMo_{12-n}V_nO_{40}]$·aq, was explained by the combination of their intrinsic Brønsted acidity together with their redox properties [39,40]. In order to obtain higher conversions, the acidity of the catalytic system was further increased *via* the addition of H_2SO_4 into the reaction mixture. It seems clear that its presence enhances the catalytic activity in the reaction of oxidative cleavage of 2-methylcyclohexanone (see entries 3–5 in Table 4). Note that a further addition in sulfuric acid (entry 6, Table 4) did not allow to improve the product yield.

It is noteworthy that for a K-10 MT sample first treated *ex situ* with sulfuric acid, a decreased conversion was observed compared to what is obtained for a test performed with K-10MT and the joint addition of sulfuric acid (see Table 4, entry 7 compared to Table 4, entries 3 and 5 and see Table 4, entries 8 and 9 compared to Table 3, entry 2). This could be explained considering that the pretreatment of K-10MT performed in acidic aqueous medium has led to a partial depletion in some cations within the octahedral sheet (please see XRF results below). Consequently, the number of protons in the interlamellar space was reduced because they balance the net negative charge on the layer which arises from isomorphous substitution in the octahedral sheet [41].

Using clay catalysts, the question of structural stability always arises. Structural evolution of recovered catalyst at the end of the reaction (carried in the presence of H_2SO_4 at 70 °C) was monitored with X-ray diffraction (Fig. 1b) and transmission electron microscopy (Fig. 2d).

As shown in Fig. 1b, the addition of sulfuric acid at 70 °C to the reaction mixture did not modify the basic structural characteristics

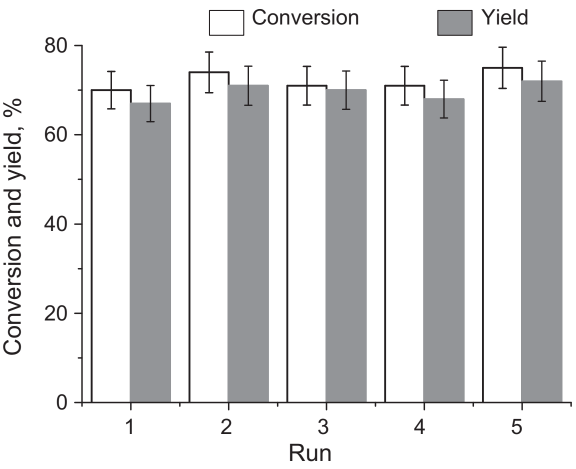


Fig. 6. Recycling of K-10MT catalyst in the oxidation of 2-methylcyclohexanone by dioxygen. Conditions: substrate (5 mmol, 0.6 mL), AcOH/H_2O (4.5 mL/0.5 mL), H_2SO_4 (0.37 mmol), K-10MT (0.2 g), *t* = 24 h, *p* (O_2) = 0.1 MPa.

of K-10MT, since the original characteristic peaks of the clay are still present. TEM image (Fig. 2d) reveals that the recovered catalyst is still laminated like the fresh clay (Fig. 2c and d). This observation is in good agreement with the X-ray diffraction results. The results given above by XRD and TEM indicate that K-10MT was not degraded under the chosen reaction conditions.

3.2.2. Catalyst regeneration

The clay obtained after the catalytic test corresponding to Table 2, entry 3 was separated at the reaction temperature from the reaction mixture by filtration and washed four times with distilled water. The resulting clay was dried at 373 K for 10 h, grounded into a fine powder and used again to study its activity for the oxidation reaction.

Fig. 6 shows that the clay can be recycled several times without any appreciable loss in activity and selectivity (the small observed variations are within the experimental error).

3.2.3. Change in the chemical composition after recycling

As it is well known [41,42], acid-activation often results in substantial changes of the montmorillonite clay such as the removal of octahedral cations or the modification of specific surface areas and pore volumes. The XRF chemical analyses (wt.%) of the fresh clay and recovered catalysts are given in Table 5. The variations of the relative content of metals (M/M_0) in the K-10MT with number of runs are given in Fig. 7 in which M_0 and M are the wt.% of the oxide elements in the fresh clay and recovered catalysts samples. Different behaviors are observed depending on the nature of the element. The relative contents of the leached elements in the K-10MT decrease in the order of Ca^{2+}, Al^{3+}, Fe^{3+}, Si^{4+}, K^+ and Ti^{4+} with the increase in number of run. There is a marked decrease in the Ca element and, to a lesser extent, in the Fe and Al elements, together with a relative increase of the Si, Ti and K elements. Similar observations have been made by Breen et al. for various smectites treated with different combinations of acid concentrations, temperatures and reaction times [41]. These results can be explained considering that the K^+ cations between 2:1 layers of montmorillonite and the Si^{4+}, Ti^{4+} cations at tetrahedral sites of smectite are not extracted from the framework by the addition of sulfuric acid in the reaction mixture. By opposition there is a partial leaching of iron and aluminum under the reacting conditions for the first four tests. After four tests, their amounts in the solid material are nearly constants. It is well known that iron(III) salts can catalyze the oxidative cleavage of cyclic ketones [43]. We thus can suspect the contribution of solvated iron species to the global catalytic activity in the first four runs. However, more importantly, the performances of the catalyst after 5 runs are the same than that of the fresh catalyst whereas the metal leaching in solution, if any, is negligible (see Figs. 6 and 7). This indicates that K-10MT can be considered as a true heterogeneous catalyst.

Table 5
X-ray fluorescence analyses of the fresh and recovered catalysts.

Run	% (w/w)					
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	K_2O
0	82.67	13.93	1.61	0.32	0.10	1.36
1	83.37	13.30	1.54	0.32	0.09	1.38
2	83.69	12.99	1.53	0.32	0.09	1.38
3	83.99	12.70	1.52	0.32	0.08	1.39
4	84.15	12.55	1.50	0.33	0.08	1.39
5	84.19	12.51	1.50	0.33	0.08	1.39

Conditions: substrate (5 mmol, 0.6 mL), AcOH/H_2O (4.5 mL/0.5 mL), H_2SO_4 (0.37 mmol), K-10MT (0.2 g), *t* = 24 h, *p* (O_2) = 0.1 MPa.

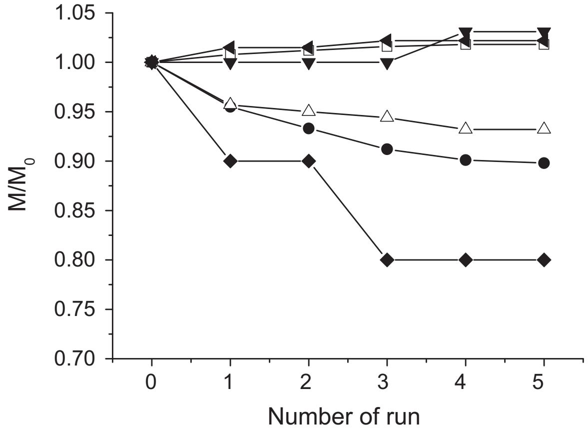


Fig. 7. Variations of the relative metal contents (M/M_0) determined by XRF for K-10MT powder *vs* the number of runs: □, Si; ♦, Ca; ●, Al; ◄, K; ▼, Ti; △, Fe.

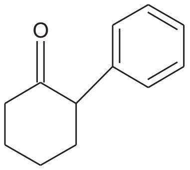
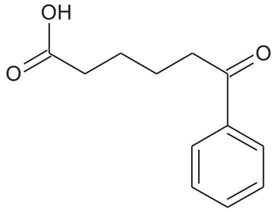
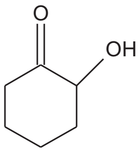
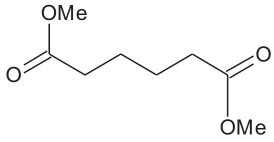
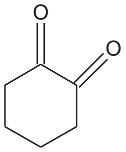
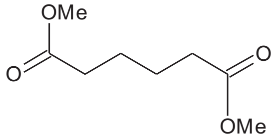
3.2.4. Oxidation of other α-substituted ketones

Encouraged by the remarkable results obtained with the above reaction conditions, and in order to show the scope and possible generalization of this new protocol, we used this catalytic system, K-10MT/AcOH-H_2O/H_2SO_4/O_2 for the oxidation of other α-substituted ketones (Table 6). 2-Phenylcyclohexanone produces mainly 5-benzoyl valeric acid (entry 1). Treatment of 2-hydroxylcyclohexanone gives adipic acid in good yield with excellent selectivity (Table 6, entry 2). Dimethyl adipate was actually obtained as a result of the *in situ* esterification of the crude mixture with methanol. Adipic acid can also been obtained from 1,2-cyclohexanedione but with a lower yield (Table 6, entry 3). In both cases, very low yields of dimetyl glutarate and dimethyl succinate derivatives were obtained.

4. Discussion

This paper describes the aerobic oxidative C—C bond cleavage of α-substituted ketones using montmorillonites as bifunctional catalysts, *i.e.* both solid and redox catalysts. Two materials were considered: a commercial montmorillonite, K-10MT, and a synthetic product, denoted S-MMT. Both solids exhibit comparable acidic properties as evidenced by NH_3 chemisorption at 373 K. Nevertheless, no conversion of the α-substituted ketone was observed

Table 6
Catalytic oxidation of α-substituted ketones by the catalytic system K-10MT/AcOH-$H_2O/H_2SO_4/O_2$.

Entry	α-Substituted ketones	mmol O_2	Conversion (%)	Product and yield (%)
1		1.85	37	 36
2[a]		2.50	50	 48
3[a]		1.30	26	 24

Conditions: substrate (5 mmol), K-10MT (0.2 g), AcOH/H_2O (4.5 mL/0.5 mL), H_2SO_4 (0.37 mmol), t = 24 h, 70 °C, p (O_2) = 0.1 MPa.

[a] Conversions and yields were determined by GC analysis after the *in situ* esterification of the crude mixture with methanol using methyl heptanoate as internal standard.

with S-MMT showing the fundamental role of transition metal species in the reaction pathway.

Montmorillonite is a 2:1 layered aluminosilicate with an octahedral sheet (predominantly aluminate) sandwiched by two tetrahedral layers (predominantly silicate). Due to the isomorphous substitution of Al^{3+} within the octahedral layer by divalent cations such as Mg^{2+} or Fe^{2+} and of Si^{4+} by Al^{3+} in the tetrahedral layer, the resulting charge deficit is balanced by the incorporation of exchangeable cations in the interlamellar space. X-ray fluorescence analyses have shown that iron and titanium are present in K-10MT whereas the synthetic montmorillonite is transition metal free.

Iron(III) has been shown to be active toward the aerobic oxidative C—C bond cleavage of α-substituted ketones [43]. The dimension of the hexagonal cavity in the tetrahedral layer is about 5 Å [44]. To the best of our knowledge, no data has been reported concerning the kinetic diameter of 2-methylcyclohexanone but for cyclohexane and trimethylbenzene, these diameters are 6.0 and 7.3 Å, respectively [45]. Thus, it appears that the physical access of the substrate to the octahedral layer is restricted. However, even if Milone et al. [32] have shown by X-ray fluorescence that Fe cations were mainly located in the octahedral sheet for K-10 montmorillonite, the ion-exchange reaction of a native sample (Fe amount: 2.0 wt.%) with a NaCl aqueous solution yielded a material with a reduction of the iron amount (Fe amount: 1.7 wt.%) as seen by X-ray fluorescence. Although it is a small diminution (0.3 wt.%), it indicates that some Fe cations could be located inside the interlamellar space of the clay and could thus be available for catalysis.

To date, titanium(IV) has not been reported as an efficient catalyst for such a reaction, but its participation in the catalytic cycle cannot be discarded. TiO_2 solids are well known to activate dioxygen under photocatalytic conditions [46]. Thus, in this work, the active species could correspond to Fe(II) and/or Fe(III) species intercalated between the clay layers and/or Ti(IV) species which are located in the tetrahedral sheet.

5. Conclusion

In summary, we have successfully developed a simple and efficient method for the synthesis of ketoacids or diacids derivatives from various α-substituted ketones using cheap and readily available K-10MT as catalyst using molecular oxygen as oxygen source. The main features of this procedure are the appreciable yields of products, the clean reaction profiles (*i.e.* the good selectivities) and the availability of the reagents at low cost and enhanced rates which makes it a useful and attractive process. The simple experimental and product isolation procedures as well as the easy recovery and reuse of the catalyst are expected to play an important role in the development of this new method. Moreover, these results open the way for the use of this inexpensive material in other applications.

Even if acidity is a necessary condition to allow the formation of the enol and the subsequent C—C bond oxidative cleavage, the presence of transition metals species is also a prerequisite. Indeed, with a transition metal-free synthetic montmorillonite prepared by hydrothermal synthesis, no conversion was observed. Future efforts will be directed to the preparation of transition metal (such as copper, iron, titanium or vanadium) containing synthetic montmorillonites *via* cation exchange procedures and to the evaluation of their catalytic properties. Further research will also develop toward elucidating the catalytic oxidation mechanism.

Acknowledgements

I. El Younssi thanks the Ministère de l'éducation nationale, de l'enseignement supérieur, de la formation des cadres et de la recherche scientifique of Morocco for the allocation grant. T. Rhadfi gratefully acknowledges the Agence Universitaire de la Francophonie and the CNRST for financial support. Thanks are due to Drs. J.-Y. Piquemal and L. Sicard for constructive discussions, for correcting the manuscript and for physicochemical analysis facilities, and to reviewers for valuable comments.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molcata.2012.07.022.

References

[1] R.C. Larock, Comprehensive Organic Transformations, second ed., Wiley, New York, 1999, pp. 1664–1669.
[2] K. Kervinen, H. Korpi, M. Leskelä, T. Repo, J. Mol. Catal. A: Chem. 203 (2003) 9–19.
[3] A.K. Suresh, M.M. Sharma, T. Sridhar, Ind. Eng. Chem. Res. 39 (2000) 3958–3997.
[4] A. Shimizu, K. Tanaka, M. Fujimori, Chemosphere: Global Change Sci. 2 (2000) 425–434.
[5] R. Floresca, M. Kurihara, D.S. Watt, A. Demir, J. Org. Chem. 58 (1993) 2196–2200.
[6] A. Atlamsani, J.-M. Brégeault, Synthesis (1993) 79–81.
[7] L. El Aakel, F. Launay, J.-M. Brégeault, A. Atlamsani, J. Mol. Catal. A: Chem. 212 (2004) 171–182.
[8] A. Cornelius, P. Laszlo, Synlett (1994) 155–161.
[9] T.-K. Huang, R. Wang, L. Shi, X.-X. Lu, Catal. Commun. 9 (2008) 1143–1147.
[10] W.E. Worrall, Clays and Ceramic Raw Materials, second ed., Elsevier Scientific, London, 1986.
[11] W.A. Deer, R.A. Howie, J. Zussman, An Introduction to the Rock-Forming Minerals, second ed., Addison-Wesley-Longman Ltd., Harlow, 1996.
[12] J.T. Kloprogge, E. Mahmutagic, R.L. Frost, J. Colloids Interface Sci. 296 (2006) 640–646.
[13] C.E. Weaver, L.D. Pollard, The Chemistry of Clay Minerals, Elsevier Scientific, Amsterdam, 1973.
[14] M.P. Hart, D.R. Brown, J. Mol. Catal. A: Chem. 212 (2004) 315–321.
[15] A. Vaccari, Catal. Today 41 (1998) 53–71.
[16] T. Cseri, S. Békassy, F. Figueras, E. Cseke, L.C. de Menorval, R. Dutartre, Appl. Catal. A: Gen. 132 (1995) 141–155.
[17] C. Cativiela, F. Figueras, J.M. Fraile, J.I. Garcia, J.A. Mayoral, Tetrahedron: Asymm. 4 (1993) 223–228.
[18] B.M. Choudary, N.S. Chowdari, M.L. Kantam, R. Kannan, Tetrahedron Lett. 40 (1999) 2859–2862.
[19] F.P.R. Crisóstomo, R. Carrillo, T. Martín, V.S. Martín, Tetrahedron Lett. 46 (2005) 2829–2832.
[20] T. Kawabata, T. Mizugaki, K. Ebitani, K. Kaneda, Tetrahedron Lett. 44 (2003) 9205–9208.
[21] F. Bigi, L. Chesini, R. Maggi, G. Sartori, J. Org. Chem. 64 (1999) 1033–1035.
[22] E.C. Taylor, C.-S. ChiangeTaylor, Synthesis (1977) 467.
[23] S. Hunig, E. Benzing, E. Lucke, Chem. Ber. 90 (1957) 2833–2840.
[24] J.-F. Roudier, A. Foucaud, Tetrahedron Lett. 25 (1984) 4375–4378.
[25] B. Labiad, D. Villamin, Synthesis (1989) 143–144.
[26] D. Fishman, J.T. Klug, A. Shani, Synthesis (1981) 137–138.
[27] M. Onaka, T. Shinoda, Y. Izumi, R. Nolen, Chem. Lett. (1993) 117–120.
[28] M. Reinholdt, J. Miehé-Brendlé, L. Delmotte, M.-H. Tuilier, R. le Dred, R. Cortès, A.-M. Flank, Eur. J. Inorg. Chem. (2001) 2831–2841.
[29] P. de Chateaubourg, J.-P. Quisefit, S. Garivait, E. Steiner, C. Goyon, Analusis 21 (1993) 293–298.
[30] R.A. Sheldon, M. Wallau, I.W.C.E. Arends, U. Schuchardt, Acc. Chem. Res. 31 (1998) 493–495.
[31] A. Bakandritsos, A. Simopoulos, D. Petridis, Nanotechnology 17 (2006) 1112–1117.
[32] C. Milone, M. Dhanagopal, S. Santangelo, M. Lanza, S. Galvagno, G. Messina, Ind. Eng. Chem. Res. 49 (2010) 3242–3249.
[33] K.S.W. Sing, D.H. Everett, R.A.W. Haul, L. Moscou, R.A. Pierotti, J. Rouquerol, T. Siemieniewska, Pure Appl. Chem. 57 (1985) 603–619.
[34] U. Flessner, D.J. Jones, J. Rozière, J. Zajac, L. Storaro, M. Lenarda, M. Pavan, A. Jiménez-López, E. Rodríguez-Castellón, M. Trombetta, G. Busca, J. Mol. Catal. A: Chem. 168 (2001) 247–256.
[35] M. Vennat, J.-M. Brégeault, Appl. Catal. A: Gen. 386 (2010) 9–15.
[36] F. Cavani, L. Ferroni, A. Frattini, C. Lucarelli, A. Mazzini, K. Raabova, S. Alini, P. Accorinti, P. Babini, Appl. Catal. A: Gen. 391 (2011) 118–124.
[37] R.M. Stephenson, J. Chem. Eng. Data 37 (1992) 80–95.
[38] I. Belkhir, A. Germain, F. Fajula, E. Fache, J. Chem. Soc. Faraday Trans. 94 (1998) 1761–1764.
[39] A. Atlamsani, J.-M. Brégeault, M. Ziyad, J. Org. Chem. 58 (1993) 5663–5665.
[40] L. El Aakel, F. Launay, A. Atlamsani, J.-M. Brégeault, Chem. Commun. (2001) 2218–2219.
[41] C. Breen, F. Deeba Zahor, J. Madejová, P. Komadel, J. Phys. Chem. B 101 (1997) 5324–5331.
[42] P. Komadel, J. Madejová, Acid activation of clay minerals, in: F. Bergaya, B.K.G. Theng, G. Lagaly (Eds.), Handbook of Clay Science. Development in Clay Science, vol. 1, Elsevier Ltd., 2006, pp. 263–288.
[43] S. Ito, M. Matsumoto, J. Org. Chem. 48 (1983) 1133–1135.
[44] C. Swearingen, J. Wu, J. Stucki, A. Fitch, Environ. Sci. Technol. 38 (2004) 5598–5603.
[45] A. Jakob, V. Valtchev, M. Soulard, D. Faye, Langmuir 25 (2009) 3549–3555.
[46] M. Dan-Hardi, C. Serre, T. Frot, L. Rozes, G. Maurin, C. Sanchez, G. Férey, J. Am. Chem. Soc. 131 (2009) 10857–10859.