Research paper

Novel vanadium-chromium-bentonite green catalysts for cyclohexene epoxidation

Noureddine Belaidi, Sumeya Bedrane, Abderrahim Choukchou-Braham [1], Redouane Bachir

Laboratoire de catalyse et synthèse en chimie organique, Faculté des Sciences, University of Tlemcen, Tlemcen 13000, Algeria

ABSTRACT

The aim of this work is the valorization of bentonite-type clay from Maghnia (Algeria) as green catalyst for the production of added value fine chemicals. The modification of the clay structure by acid activation and impregnation of transition metals, such as chromium and vanadium, enhanced redox properties and increased Lewis and Brønsted acidity. Various samples of vanadia supported on chromium-containing acid-activated bentonite, were prepared and characterized by diffuse-reflectance UV–vis spectroscopy, surface acidity followed by FT-IR, X-ray diffraction, nitrogen adsorption–desorption isotherms and scanning electron microscopy (SEM) coupled with EDX. The catalysts prepared were studied in the cyclohexene epoxidation, using tert-butyl hydroperoxide as oxidant. The influences of vanadium content, catalyst weight, reaction temperature and oxidant amount on the evolution of the epoxidation reaction were checked. The experimental results showed an interesting catalytic activity of 43% and a selectivity towards epoxide of about 71%, when TBHP was used as oxidant and heptane as solvent.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Clay minerals have been commonly used in industry and laboratory applications, either in their natural forms or after modification. Clay minerals as catalysts have attracted increasing attention from researchers as they represent a class of materials whose porosity and acidity may be adapted after special treatments (Adams and McCabe, 2006). Acid attack is a useful method to modify the catalytic behavior and the acidity of the clay (Ravichandran and Sivasankar, 1997; Komadel and Madejova, 2006). Acid-activated clay minerals have wide industrial applications such as radioactive waste disposal (Wang et al., 2010), removal of heavy metals from industrial wastewaters (Kennedy Oubagaranadin et al., 2010) and catalysts (Chitnis and Sharma, 1997). Many works reported the catalytic activities of acid-activated clays in several organic reactions (Khedher et al., 2006; Dutta et al., 2011; Paul et al., 2011).

Moreover, transition metal oxides are known for their redox properties and their capacity to catalyze the oxidation of hydrocarbons, such as vanadium and chromium (Gould and Rado, 1969; Anisimov et al., 2003; Bolm, 2003; Ligtenbarg et al., 2003; Shylesh et al., 2007). Catalytic epoxidation of alkenes is an important industrial reaction and a useful synthetic method for the production of a wide variety of fine chemicals because they are directly derived from alkenes, a primary petrochemical source. Epoxides are versatile intermediates in organic synthesis because they can easily undergo ring-opening to form mono- or bi-

functional compounds (Augustine, 1996). Generally, epoxides can be formed from corresponding alkenes by oxidation at laboratory and industrial scale. The epoxidation of cyclohexene has been widely investigated using several metal catalysts under homogeneous and heterogeneous conditions (Qiu et al., 2009; Salavati-Niasari et al., 2011; El-Korso et al., 2012; Lahcene et al., 2012; Ameur et al., 2013). It was shown (Xiaoli et al., 2011) that cyclohexene epoxidation, with H_2O_2 as oxidant over immobilized chromium Schiff base complexes, leads to a cyclohexene conversion of 52.6% and an epoxide selectivity of 73.5%. In addition, it is well known that vanadium is an efficient catalyst in various organic reactions (Hirao, 1997). Recently, many works have investigated its catalytic activity either as oxovanadium homogeneous complexes or as supported catalysts in epoxidation reactions (Parida et al., 2010; Yang et al., 2011; Das and Parida, 2012; Grivani et al., 2012; Leus et al., 2012; Mikolajska et al., 2012). Several mechanisms have been proposed for the oxidation reactions. In one hand, the Mars and van Krevelen mechanism, proposed by Corma and Garcia (2002) states that the oxidation reactions are managed by a number of Lewis acid, Lewis basic and redox centers. On the other hand, Busch et al. (2008) suggest another mechanism involving Lewis acids for the epoxidation of olefins.

This paper aims to elaborate a new combination of materials, involving the redox properties of both vanadium and chromium and the acidity of activated bentonite in order to improve the catalytic activity and propose an appropriate reaction pathway. The prepared catalysts were tested in cyclohexene epoxidation with TBHP as oxidant and heptane as solvent. The effects of various reaction parameters such as the catalyst weight and the reaction temperature were checked. The catalytic materials were widely characterized by diffuse-reflectance UV–vis

spectroscopy, X-ray diffraction, surface acidity followed by FT-IR spectroscopy, nitrogen adsorption–desorption isotherms and scanning electron microscopy coupled with energy-dispersive X-rays (SEM-EDX) in order to correlate their physico-chemical features to the catalytic performances.

2. Experimental

2.1. Raw materials and catalysts preparation

Bentonite clay from Maghnia (Algeria) was used in this work. The raw material was purified by dispersion in water, careful decantation and extraction of the fraction with particle size smaller than 2 μm. The structural formula of purified bentonite, based on chemical analysis, was found to be [SiO_2, 61%; Al_2O_3, 16.1%; Fe_2O_3, 2.8%; Na_2O, 1.5%; MgO, 3.53%, TiO_2, 0.22%; K_2O, 1.6%; CaO, 3.15%; MnO, 0.04%; H_2O, 10.16%]. The cation exchange capacity (CEC) was 0.95 mEq g^{-1} and the basal spacing 13.8 Å. In order to obtain the acid-activated clay, noted AAC, the parent bentonite was dispersed in a solution of HCl (1.0 M) and vigorously stirred at 80 °C for 4 h. Then the bentonite was separated from the solution and washed with distilled water until complete removal of chloride anions (test reaction with $AgNO_3$). This procedure was repeated 3 times.

The incorporation of chromium polycations was carried out following the procedure previously described (Tzou and Pinnavaia, 1988). According to this procedure, a solution of $Cr(NO_3)_3$, 9 H_2O (0.1 M) (Aldrich, purissimum) was hydrolyzed at 65 °C with a solution of Na_2CO_3 (0.1 M) (Panreac, purissimum), at an OH/Cr^{3+} molar ratio of 2.0. The obtained solution was aged for 1 h at the same temperature so that precipitation could take place. It was then added to a previously prepared dispersion of acid-activated bentonite in water with 10 mmol Cr per gram of clay. The resulting slurry was left under stirring for 24 h to favor to favor chromium species incorporation and then washed with distilled water until elimination of nitrates. The resulting solid was separated by centrifugation and dried at 80 °C for 16 h. Finally, it was calcined at 300 °C for 3 h to obtain chromium-containing acid-activated clay, noted Cr-AAC.

Samples containing 5, 10 and 15 wt.% of vanadium were prepared at room temperature, under vigorous stirring, by the incipient wetness impregnation of chromium-containing acid clay support (Cr-AAC) with an adequate aqueous solution of NH_4VO_3 dissolved in oxalic acid (0.1 M) (Bahranowski et al., 1997). All the samples were dried at 80 °C for 20 h and calcined at 500 °C for 5 h. These catalysts will be noted xV/Cr-AAC (where x is the vanadium loading).

2.2. Characterization methods

Diffuse-reflectance UV–visible spectra (200–800 nm) of these samples were collected upon a Perkin-Elmer Lambda 800 UV/vis spectrophotometer equipped with a diffuse reflectance accessory set to collect the diffuse reflected light only. The baseline was recorded using $BaSO_4$ as a reference material.

The specific surface area, pore and micropore volumes of the samples were determined from N_2 adsorption isotherms at 77 K using a Quantachrome Nova 1000^e instrument. The pore size distribution was calculated by the BJH method from the desorption branch. The surface area and micropores volume were calculated using the t-plot-De Boer method. Prior to physisorption measurements, the samples were out gassed at 250 °C for 3 h, under vacuum.

The FT-IR spectra of modified Montmorillonite clay catalysts were recorded, at room temperature, on a Cary 640 FT-IR spectrometer. The catalyst sample (~50 mg) were mixed with KBr and pressed in a self-supported disk, dried in a hot oven at 100 °C for 1 h, evacuated and then cooled down to the room temperature. The sample was brought into direct contact with a known amount of pyridine (~0.1 cm^3). The sample disk was heated in an oven at 120 °C for 1 h, to remove the physisorbed pyridine. After cooling down the catalyst sample, the IR spectrum was recorded, in the spectral range from 1650 to 1350 cm^{-1} with a 4 cm^{-1} resolution, using a KBr background.

X-ray powder diffractograms (XRD) were recorded on a Rigaku D/max 2500 diffractometer with Ni-filtered Cu Kα radiation (λ = 1.541874 Å), between 2.5 and 70° (2θ), at a scanning speed of 1 step per second (step size = 0.03°).

The scanning electron microscopy (SEM) coupled with EDX (energy-dispersive X-rays) analysis was performed using a Hitachi-TM.1000 at a 150 KV acceleration voltage.

2.3. Catalytic experiments

The catalytic epoxidation of cyclohexene with tert-butyl hydroperoxide (TBHP) (Aldrich 70 wt.% in H_2O) as an oxidant was carried out in a two-neck glass round-bottom flask equipped with a magnetic stirrer and a reflux condenser or in an autoclave at atmospheric pressure. First, TBHP was stirred with n-heptane as solvent in order to perform a transfer from water phase to organic phase. Typically, 20 mL of n-heptane and 38.45 mmol (5.5 mL) of oxidant (TBHP) were mixed in a closed Erlenmeyer flask and magnetically stirred for 24 h. The organic phase was then separated from the aqueous phase. To control the phase transfer, the concentration of the remaining TBHP in the aqueous phase was regularly determined by iodometric titration. Less than 10% of the initial TBHP remained in the aqueous phase. Twenty-nine millimoles (3 mL) of cyclohexene was added to the TBHP–heptane mixture, which was afterwards heated to 70 °C under vigorous stirring. At time zero, 100 mg of the catalyst was added to the previous mixture. The reaction products were followed by gas chromatography (GC), using a SCHIMADZU GC 14-B equipped with the capillary column "Agile HP-FFAP" and flame ionization detector (FID). Before GC analysis, the remaining TBHP was decomposed by introducing an excess of triphenylphosphine (Aldrich). On the other hand, in order to control the remaining TBHP, an iodometric titration was performed at the end of the reaction (after 6 h) by analyzing the organic phase:

$$\text{Conversion (\%)} = 100 \times \frac{[C_6H_{10}]_0 - [C_6H_{10}]_t}{[C_6H_{10}]_0}$$

$$\text{Selectivity (\%)} = 100 \times \frac{\text{moles of individual product}}{\text{moles of total products}}$$

3. Results and discussion

3.1. Materials characterization

The DR UV–vis spectra are given in Fig. 1. The AAC spectrum displays a characteristic broad band centered at about 250 nm, which is due to the ($Fe^{3+} \Longleftarrow O^{2-}$, OH^- or OH_2) charge–transfer band due to iron in the octahedral layer of the clay (Arfaoui et al., 2010). The DR UV–vis spectrum of Cr-AAC shows two characteristic bands, at 260 nm and 364 nm, due to the charge transfer $Cr^{6+} \Longleftarrow O^{2-}$, which indicates that chromium is tetrahedrally coordinated (Mishra and Parida, 1998). In the case of 5V/Cr-AAC, the spectrum is dominated by two charge-transfer (CT) bands of V^{5+} at 260 and 360 nm. It has been reported that, for V^{5+} oxoanions (3 d^0), a very strong absorption due to the CT transition between oxygen ligands and central V atoms is generally observed in the UV–vis region (Iwamoto et al., 1983; Morey et al., 1996). Accordingly, the band observed below 300 nm may be due to the low-energy ligand-to-metal (O^{2-} to V^{5+}) charge-transfer (LMCT) transitions associated with the isolated tetrahedral monomeric species and the band around 350–400 nm to the polymeric vanadia chains (Held and Florczak, 2009; Bineesh et al., 2010). These polymeric species are formed by V–O–V bridges upon isolated tetrahedral vanadium species. An absorption band around 480 nm was observed, indicating the presence of bulk-like crystalline vanadia species (Grygar et al., 2009; Held