Journal of Molecular Catalysis A: Chemical 377 (2013) 42–50

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Catalysis A: Chemical

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

Characterization and performance of the bifunctional platinum-loaded calcium-hydroxyapatite in the one-step synthesis of methyl isobutyl ketone

Najwa Takarroumt [a], Mohamed Kacimi [a], François Bozon-Verduraz [b], Leonarda F. Liotta [c], Mahfoud Ziyad [a,*]

[a] Université Mohammed V-Agdal, Faculté des Sciences, Laboratoire de Physico-chimie des Matériaux et Catalyse, Département de Chimie, Avenue Ibn Battouta, B.P. 1014, Rabat, Morocco
[b] Groupe Nanomatériaux, ITODYS, UMR-CNRS 7086, Université Paris-Diderot (Paris 7), Bâtiment Lavoisier, 15, rue Jean-Antoine de Baïf, 75205 Paris Cedex 13, France
[c] Istituto per Lo Studio dei Materiali Nanostrutturati (SMN)-CNR, via Ugo La Malfa 153, 90146 Palermo, Italy

ARTICLE INFO

Article history:
Received 31 July 2012
Received in revised form 22 March 2013
Accepted 18 April 2013
Available online 30 April 2013

Keywords:
Platinum loaded calcium-hydroxyapatite
Butan-2-ol conversion
Methyl isobutyl ketone (MIBK)
Diffuse reflectance spectroscopy
Temperature programmed reduction

ABSTRACT

Calcium-hydroxyapatite catalysts loaded with different amounts of platinum Pt(*x*)/CaHAp were synthesized and characterized by N_2-adsorption, X-ray diffraction, transmission electron microscopy, Fourier transform infrared, ultraviolet–vis–NIR spectroscopy and temperature programmed reduction. It was found that the loaded platinum was mainly exchanged and dispersed on the apatite surface, forming particles with an average size of 2 nm. The exchanged platinum, as shown by XRD, did not affect the apatite structure or its crystallinity. The specific surface area of the bare CaHAp as well as the mean pore diameter, diminished by increasing the Pt loading, probably because the pores were partially blocked. The Pt(*x*)/CaHAp samples calcined at 500 °C contained, beside the exchanged platinum, Pt and PtO. H_2-TPR results showed that the platinum occupied on the apatite at least two different sites.

The acid–base and redox properties of the catalysts were studied using, as the probe reaction, butan-2-ol conversion. The impregnation of CaHAp with Pt decreased its natural basic properties and enhanced markedly the dehydrogenation of butan-2-ol into methyl ethyl ketone (MEK). In the presence of air, the production of MEK increased abruptly with the temperature. The reaction started at 30 °C, passed through a maximum (90% of conversion) at 60 °C and then it decreased rapidly. This important activity at low temperatures was attributed to Pt and Pt^{2+} species associated with the basic Ca^{2+}–O^{2-} groups of the apatite.

The synthesized bifunctional catalysts were also investigated in the acetone conversion, in one step, into methyl isobutyl ketone (MIBK). The optimal performance was achieved with the sample loaded with 0.5 wt.% Pt. It displayed at 150 °C and stationary state a MIBK yield of 23% with a selectivity of 74%. Moreover, all the Pt(*x*)/CaHAp catalysts showed an acceptable stability over time on stream with no production of heavy compounds.

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1. Introduction

Methyl isobutyl ketone (MIBK or 4-methyl-2-pentanone) is produced on industrial scale to be used mainly as solvent for paint, varnishes, adhesives, and pesticides and also for the extraction in pharmaceutical industry and the separation of metals such as zirconium from hafnium [1]. The world production capacity of MIBK in 2005 was around 366,000 tonnes, mostly manufactured by homogeneous catalysis using a three-step process in aqueous phase [2]. The first step of the reaction consists in a self-condensation of acetone in diacetone alcohol (DAA, 4-hydroxy-4-methyl-2-pentanone) on basic sites. In the second step, the DAA undergoes dehydration on acid sites leading to mesityl oxide (MO, 4-methyl-3-penten-2-one). The last step is the selective hydrogenation of the C=C double bond of MO, instead of C=O, leading to MIBK. The use of homogeneous base and acid catalysts has, however, inconveniences consisting in side reactions such as unselective hydrogenation (formation of methyl isobutyl carbinol, MIBC), over-condensation (formation of triacetone dialcohol...), high operating pressure, reversibility of the second step and generation of significant quantities of salt waste from catalyst neutralization in addition to corrosion problems. For all these reasons, particular attention has been devoted in recent years to the search of heterogeneous multifunctional catalysts containing acid–base and metal functionalities, capable of carrying out all three reactions in a single step. Heterogeneous catalysts also have the advantage of being reusable, with the possibility of regeneration.

* Corresponding author. Tel.: +212 628502304; fax: +212 628502304.
E-mail addresses: ziyad@fsr.ac.ma, mahfoudziyad@gmail.com (M. Ziyad).

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http://dx.doi.org/10.1016/j.molcata.2013.04.017

Several papers have been published on single step synthesis of MIBK in gas phase over Ni supported on Al_2O_3 [3], ZnO [4], CaO [5], MgO [6], hydrotalcite [7], zeolites [8], carbon [9], Cu/MgO [10], palladium dispersed on ZrP [11], ZSM-5 [12], Cu/MgAlO [13], PtCu/H[Al]ZMS5 [14] and recently on $Pt/SiO_2–ZrO_2$ [15]. The results show that the selectivity is generally below 80%, mainly because the consecutive hydrogenation of acetone leads to the production of isopropyl alcohol (IPA) and propylene. On the other hand, the catalysts dispersed on acid carriers do not exhibit a very good stability. Such supports favour the formation of carbonaceous deposits, which provoke a rapid poisoning of the active sites. The use of less acid or slightly basic carriers improves to some extent the stability of the catalysts. Chikán *et al*. reported a stable production of MIBK for 24 h over Cu/MgO [10,13].

Calcium-hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$, named here CaHAp, has basic features and exchange properties and was found to be an excellent new basic catalyst for Michael addition reactions [16]. The structure of $Ca_{10}(PO_4)_6(OH)_2$ possesses great flexibility in accepting substitutions in its network and cationic exchanges (Ca^{2+}/M^{2+}) which modulate its acid–base and catalytic properties [17–19]. The framework of $Ca_{10}(PO_4)_6(OH)_2$ can be described as a compact assemblage of tetrahedral $(PO_4)^{3-}$ groups which delimit two types of channels with diameters of 2.5 Å and 3.5 Å, bordered by oxygen atoms and Ca^{2+} ions. The $(OH)^-$ hydroxyls are hosted by the largest channels. These hydroxyls play a special role because they can be substituted by anions of similar size [20]. Moreover, as reported in the literature, these hydroxyls can be converted into active oxygen species, which intervene in the catalytic abilities of CaHAp [21]. Except for two reports on ZrP [11] and aluminophosphate oxynitride [22], respectively, phosphates have not been used as carriers for one-step synthesis of MIBK. The only report we know about is the work carried out by some of us over Pd(*x*)/CaHAp catalysts [23].

The present study is devoted to the synthesis of MIBK, in one step, over Pt loaded CaHAp. Platinum was chosen because of its good performance in a large variety of hydrogenation reactions and the phosphate because phosphorus is often added to the catalysts in order to promote their activity and prevent their inhibition by carbonaceous deposits [14,15]. With this aim, several catalysts of Pt(*x*)/CaHAp, loaded with different amount of Pt, were synthesized and characterized by various techniques including butan-2-ol conversion for the acid–base features. Special attention was given to the search of correlations between the structural properties of Pt(*x*)/CaHAp and their catalytic activity in both reactions.

2. Experimental

2.1. Catalysts synthesis

Calcium-hydroxyapatite (CaHAp) was prepared by pouring, drop wise, 100 mL of $(NH_4)_2HPO_4$ (0.06 M) into 100 mL of $Ca(NO_3)_2.4H_2O$ (0.1 M) at pH = 9 adjusted by ammonia addition [24]. The mixture was maintained under stirring for 1 h, then, heated overnight at 80 °C. The obtained precipitate was filtrated, washed with ultrapure hot water to eliminate traces of nitrates and dried at 100 °C for 24 h before being calcined at 500 °C for 2 h in air.

The impregnation of CaHAp was carried out at room temperature using solutions containing different concentrations of tetramine platinum chloride, $Pt(NH_3)_4Cl_2{\cdot}nH_2O$. The resulting catalyst was dried until the complete evaporation of water and, then, calcined at 500 °C overnight. Samples containing 0.25, 0.5, 1, 1.5, 2 and 2.5 wt.% of Pt were prepared and labelled Pt(*x*)/CaHAp (where *x* is the wt.% of Pt determined by the analysis of the samples).

2.2. Characterization techniques

The so prepared Pt catalysts and the CaHAp oxide were examined using different techniques. Calcium content was determined by atomic absorption and phosphorus by colorimetric technique with a precision of ±10%. Platinum content was determined by inductive coupling plasma atomic emission spectroscopy (ICP-AES).

The BET specific surface areas of the samples calcined at 500 °C and evacuated for 2 h at 300 °C were determined by equilibrium adsorption and desorption isotherms of N_2 at 77 K with a GEMINI 2360 type apparatus. The mean pore diameter and the pore volume were calculated by BJH method.

X-ray diffraction patterns were obtained with a Siemens D5000 high-resolution diffractometer using a cobalt anticathode ($\lambda = 1.788$ Å). The data were collected at room temperature with a 0.02° step size in 2θ, from $2\theta = 20–80°$. The crystalline phases were identified by comparison with ICSD reference files [25].

The nanometric morphology of the catalysts was investigated using a JEOL 100 CX II transmission electron microscopy (TEM). The observations were made on samples dispersed in an ethanol solution deposited on a cooper grille coated with a thin layer of carbon.

Fourier transform infrared (FTIR) spectra were recorded between 400 cm^{-1} and 4000 cm^{-1} at room temperature on a Bruker Equinox 55 spectrometer using self-supporting KBr disks. This technique, which is very sensitive to the presence of carbonates and pyrophosphates, was used to provide information about the apatite purity and the modifications it undergoes while loading it with platinum.

Ultraviolet–visible–near infrared (UV–vis–NIR) diffuse reflectance spectra were recorded at room temperature between 190 nm and 2500 nm on a Varian Cary 5E spectrometer equipped with a double monochromator and an integrating sphere coated with polytetrafluoroethylene (PTFE). PTFE was also used as the reference.

Temperature programmed reduction (H_2-TPR) experiments were performed on the calcined Pt(*x*)/CaHAp catalysts, by using an home-made apparatus equipped with a U-shaped quartz reactor, operating at atmospheric pressure and loaded with 50 mg of the catalyst sieved to a grain size ranging from 120 μm to 180 μm. Hydrogen uptake was calculated by thermal conductivity detector (TCD) analysis, through appropriate calibration curves. Special attention was paid to the experimental conditions in order to avoid recording artefacts [26]. The reaction mixture was composed by 5 vol.% of H_2 and 95 vol.% of argon in a total flow rate of 25 $cm^3\,min^{-1}$. Prior to the H_2-TPR experiments, the samples were treated under oxygen at 500 °C. The reactor temperature was increased from the ambient up to 800 °C, with a heating rate of 5 °C min^{-1}.

2.3. Catalytic tests

2.3.1. Butan-2-ol conversion

The catalytic tests were carried out at temperatures between 30 °C and 240 °C in a continues-flow Pyrex microreactor. Prior to the tests, the catalyst (20–50 mg) was treated at 500 °C under 60 $cm^3\,min^{-1}$ of air then cooled to the reaction temperature. Butan-2-ol at a partial pressure of 8.4×10^2 Pa was supplied to the reactor by a saturator maintained at a 10 °C and fed with N_2 or air at a total flow rate of 60 $cm^3\,min^{-1}$. The reaction products were analyzed using two on-line chromatographs: one operating with a FID detector and a 4 m column packed with Chromosorb PAW coated with 15% of carbowax 1500 for the alcohol and methyl ethyl ketone separation, and the other one

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