C. R. Chimie xxx (2017) 1–10

Contents lists available at ScienceDirect

Comptes Rendus Chimie

www.sciencedirect.com

Full paper/Mémoire

Solid-phase and precipitation synthesis of Ti-pyrophosphate for the catalytic oxydehydrogenation of *n*-butane

Ezzina Mokrane [a, b, *], Siham Barama [a], Akila Barama [a, **], Fathelrahman Hamid Alhassan [c], Yun Hin Taufiq-Yap [d], Hassiba Messaoudi [a], Samira Slyemi [a], Ludovic Pinard [e]

[a] *Laboratoire des matériaux catalytiques et catalyse en chimie organique (LMCCCO), Faculté de chimie, USTHB, BP32 EL Alia 16123 Bab Ezzouar, Alger, Algeria*

[b] *Département des sciences alimentaires et nutrition humaine, Faculté des sciences de la nature et de la vie, Université Hassiba-Ben-Bouali-Chlef (UHBC), 02002, Chlef, Algeria*

[c] *Department of Chemistry, Faculty of Science, Qassim University, Buraydah, Saudi Arabia*

[d] *Catalysis Science and Technology Research Centre, Faculty of Science, Universiti Putra Malaysia, Selangor, Malaysia*

[e] *Institut de chimie des milieux et matériaux de Poitiers (IC2MP), Université de Poitiers, 40, av. du Recteur-Pineau, 86022, Poitiers cedex, France*

ARTICLE INFO

Article history:
Received 3 May 2017
Accepted 17 August 2017
Available online xxxx

Keywords:
Pyrophosphate
TiP_2O_7 phase
Nanoparticles
ODH of *n*-butane
Butadiene

ABSTRACT

In this article, the effect of the preparation methods of titanium pyrophosphate (TiPO) catalysts on their catalytic performances via the oxydehydrogenation (ODH) of *n*-butane has been investigated. The TiPO-A, TiPO-B, and TiPO-S catalysts have been prepared, respectively, by three synthesis methods: (1) liquid–solid, (2) coprecipitation, and (3) solid-state methods. The samples have been characterized by N_2-sorption, X-ray diffraction, inductively coupled plasma through the atomic emission spectroscopy, Fourier transform infrared, thermogravimetric analysis, differential scanning calorimetry, field emission scanning electron microscopy, and temperature-programmed desorption (NH_3 or CO_2). Fourier transform infrared and X-ray diffraction data indicate the presence of a pure TiP_2O_7 phase in TiPO-A and TiPO-S samples, whereas TiPO-B revealed the presence of an amorphous TiP_2O_7 and rutile TiO_2 phase. The coupled TGA/DSC curves showed that all catalysts are stable up to 600 °C. The catalytic testing, performed at 500 °C in ODH of *n*-butane, shows that the best yield (11.6%) is obtained over the TiPO-A catalyst, with 22.7% of butane conversion and 51.2% of total butene selectivity (whose 94.6% is the *trans*-2-butene), and seems to be an important result in this work. Only the TiPO-B1 catalyst produced butadiene with 1.7% (14.2% of ODH product) selectivity; this result is no less crucial.

1. Introduction

Recently, diverse applications of the phosphates and pyrophosphate in the domain of catalysis, photocatalysis, and adsorption have become the subject of extensive investigations, owing to their interesting physicochemical and textural properties. Pyrophosphates have interesting properties particularly in industrial and environmental applications [1–7]; indeed, these materials are used as conditioning matrices for radioactive waste [1] and fuel cells [2]. They are very attractive in heterogeneous catalysis and are used in Beckmann rearrangement [3], dehydration and oxydehydration of glycerol [4,5], xylose to furfural, [6] and sorbitol to isosorbide [7] and also in selective oxidation of low alkanes [8–11], and widely used in

---

* Corresponding author.
** Corresponding author.
E-mail addresses: zinamokrane@gmail.com (E. Mokrane), a_barama@yahoo.fr (A. Barama).

http://dx.doi.org/10.1016/j.crci.2017.08.001

Please cite this article in press as: E. Mokrane, et al., Solid-phase and precipitation synthesis of Ti-pyrophosphate for the catalytic oxydehydrogenation of *n*-butane, Comptes Rendus Chimie (2017), http://dx.doi.org/10.1016/j.crci.2017.08.001

oxydehydrogenation (ODH) of alkanes such as isobutane [12–15] and *n*-butane [16–21]. They have moderately active lattice oxygen [12,13] and moderate acidic properties, whose strength depends on the metal bond and preparation method [4].

The titanium pyrophosphate (TiPO) structure can be described as a network of corner-sharing TiO_6 octahedra with P_2O_7 double-tetrahedra units, characterized by the presence of intersecting tunnels delimited by pentagonal forms. TiP_2O_7 has a cubic structure, which can be thought as NaCl-type arrangement of Ti^{4+} and $(P_2O_7)^{4-}$ ions. This unique crystalline structure is, indeed, able to act as a Li-ion insertion host, showing reversible insertion and extraction of Li-ion under a certain electric potential [22].

Light alkanes are easily obtained from liquefied petroleum gas and frequently used as a feedstock in the production of petrochemical intermediates. The valuable compounds like alkenes are produced from the dehydrogenation process of light alkanes. This reversible endothermic process is due to the required high temperature. However, in the ODH of light alkanes, the molecular oxygen reacts with alkanes to form alkenes and water; therefore, the ODH process is exothermic and operates at temperatures generally less than 600 °C [23]. However, the obtained olefins, more reactive than the alkanes, could undergo a total oxidation. Many recent studies of diverse materials tested in catalytic oxidative dehydrogenation of *n*-butane have been reported in the literature, that is, carbon nanotubes modified by phosphates [24], Bi–Mo–V oxides [25], $V_2O_5/MO{-}Al_2O_3$ heterogeneous catalysts [26], Bi–Ni–O/γ-alumina [27], Pt/Sn/M/γ-alumina (M = Zn, In, Y, Bi, and Ga) [28], and $Mg_3(VO_4)_2/MgO{-}ZrO_2$[29]. Coprecipitation synthesis of TiPO using sodium pyrophosphate is interesting and provides high reactivity materials in catalytic ODH of isobutane [15]. It could exhibit the best catalytic activity and selectivity for the ODH of *n*-butane.

In this study, much attention is given to the synthesis routes owing to study a new preparation scheme of TiPO via a solid-state technique (by dry way), because it is a simple and fast method and gives a pure phase and promising results with a well-ordered structural aspect and a rosette-shaped texture. The objective of this article is to prepare the TiPO catalyst through solid-state scheme, liquid–solid reaction, and coprecipitation methods. The prepared catalysts are characterized by several physicochemical techniques and their catalytic activities have been assessed via an ODH of *n*-butane for investigation of the selectivity toward the products.

2. Experimental section

2.1. Catalysts preparation

Various TiPO with theoretical molar ratio P/Ti = 2 are prepared using three different synthesis methods. The TiPO catalysts are denominated TiPO-M (where M refers to the method of synthesis) and then labeled as follows: (1) TiPO-A (A, liquid–solid), (2) TiPOB (B, coprecipitation), and (3) TiPOS (S, solid-phase). The three obtained samples are very fine powders with white color. The protocol of three syntheses is described in the following section.

2.1.1. Method A (TiPO-A sample)

This technique is performed in two steps [16,18,30,31]. In the first step, the titanium dioxide (TiO_2) is prepared by a precipitation method of titanium hydroxide precursor $Ti(OH)_4$ from titanium tetrachloride ($TiCl_4$; Merck 99%), and then followed by calcination at 450 °C during 4 h. In the second step, the TiO_2 is dispersed in ultrapure water with the appropriate amount of phosphoric acid (85%). The obtained mixture is maintained at 120 °C overnight. The obtained precursor is crushed and calcined in air at 600 °C for 3 h. The formation of TiPO particles through dehydration of TiO_2 and phosphoric acid in aqueous solution is described by the following proposed equation:

$$TiO_2 + 2H_3PO_4 \rightarrow TiP_2O_7 + 3H_2O\ (postcalcination) \tag{1}$$

2.1.2. Method B (TiPO-B sample)

Sodium pyrophosphate ($Na_4P_2O_7$) solution (0.1 M) is added dropwise to an acidified solution (0.1 M) of $TiCl_4$ (Merck 99%), in a stoichiometric ratio P/Ti = 2, using lactic acid (B1) and hydrochloric acid (B2) [12–15]. The pH is adjusted with nitric acid (pH = 6). The precipitate is centrifuged, filtered, washed with ultrapure water, and dried overnight, then crushed and calcined in air at 600 °C for 3 h according to the literature conditions to obtain, respectively, TiPO-B1 and TiPO-B2 samples. In this synthesis, hydrolysis is regarded as an electrostatic reaction between titanium ions (Ti^{4+}) and phosphates ions ($P_2O_7^{4-}$). The electrostatic contribution to the reaction rate can be expressed as proposed below:

$$\begin{aligned} &TiCl_4 + Na_4P_2O_7 \cdot 10H_2O \rightarrow TiP_2O_7 + 4NaCl \\ &\quad + 10H_2O\ (precipitation\ then\ calcinations) \end{aligned} \tag{2}$$

2.1.3. Method S (TiPO-S sample)

In an appropriate stoichiometric amounts, a mass of TiO_2 is mixed with a mass of diammonium hydrogen phosphate [$(NH_4)_2HPO_4$] for a solid-state reaction. The mixture was vigorously ground in an agate mortar for 20 min and then dried at 120 °C for 7 days (168 h). Finally, the mixture was calcined in air at 600 °C for 3 h [32–34]. The synthesis is described according the following proposed reaction:

$$\begin{aligned} &TiO_2\ +\ 2(NH_4)_2HPO_4\ \rightarrow\ TiP_2O_7\ +\ 4NH_3\uparrow \\ &\quad +\ 3H_2O\ (postcalcination) \end{aligned} \tag{3}$$

2.2. Catalysts characterization

The surface areas are calculated by nitrogen adsorption at 77 K temperature, according to the Brunauer–Emmet–Teller (BET) method [35], using a Micromeritics' Tristar instrument. Samples (50 mg) are degassed under primary vacuum at 90 °C for 1 h and then under secondary vacuum at 250 °C for 4 h. The BET formula is used to obtain the surface area in the relative pressure range 0.1–1. The total

Please cite this article in press as: E. Mokrane, et al., Solid-phase and precipitation synthesis of Ti-pyrophosphate for the catalytic oxydehydrogenation of *n*-butane, Comptes Rendus Chimie (2017), http://dx.doi.org/10.1016/j.crci.2017.08.001