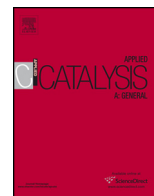




Contents lists available at ScienceDirect

Applied Catalysis A: General

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



Influence of the nature of the rare earth element in rare earth orthophosphate used for light alcohol dehydration

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ARTICLE INFO

Article history:

Received 16 October 2014

Received in revised form 5 December 2014

Accepted 10 December 2014

Available online xxx

Keywords:

Alcohol dehydration

Acid catalysts

Rare earth phosphates catalysts

Alkenes

ABSTRACT

La, Nd, Sm and Gd rare earth orthophosphates with a Rhabdophane-type structure have been synthesized and tested as catalysts for the dehydration of ethanol and 1-butanol. These solids appear to be very active and selective. Contrary to a previously studied LaPO₄ series of catalysts, whose properties were shown to depend on their P/La surface ratio, this series of rare earth phosphates exhibits catalytic properties depending mainly on the nature of the rare earth elements themselves. The most efficient phosphates presented moderately strong Brønsted and Lewis acid sites and only small quantities of weak basic sites. These properties lead to an exceptionally high selectivity to alkenes for both studied dehydration reactions. Although a good correlation was observed between the Lewis acidity and the rate of ethanol conversion, a possible involvement of Brønsted acid sites, the strength of which increases with that of the Lewis sites, cannot be totally excluded. The results of the catalysts characterization are interpreted in terms of the possible nature of the different sites.

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1. Introduction

A promising approach to the manufacture of biomass-sourced chemicals is the catalytic dehydration of light alcohols, leading to the production of various alkenes. The corresponding processes lead to lower CO₂ emissions, low production costs, and require less energy than the present refinery's processes [1]. Although many solid acid catalysts are efficient in catalyzing the dehydration of light alcohols, for industrial applications they should be usable in the presence of large quantities of water, be coke resistant, and exhibit almost total selectivity to the alkenes. If the first two requirements can be met, the last of these is more difficult to achieve. Phosphates based catalysts have been shown to be efficient and to fulfill this last requirement [2–6]. In this respect, we have recently shown that lanthanum phosphates fulfill all requirements and are ultra-selective in several mono-alcohol dehydration reactions [7]. These results were in agreement with the pioneering work of K. Ramesh et al. [8,9], although these authors obtained high catalytic properties in the case of ethanol dehydration only, for solids with a bulk P/La ratio equal to 2.

The lanthanum phosphate tested in our previous study presented Brønsted and Lewis acid sites of mainly weak or moderate strength, and only very small quantities of weak basic sites [7]. These acid–base properties resulted in the prevalence of the E₁-type mechanism for 1-butanol dehydration. Brønsted acid sites, were shown to be the most efficient. They were related to the presence of an excess of phosphorus at the surface and, from spectroscopic data, attributed to sub-surface (H_nPO₄)^{−3+n} (n = 1 or 2) species. Their prevalence and optimum distribution at the surface seems to make the catalysts extraordinarily efficient in light alcohol dehydration reactions.

Furthermore, apart from their high intrinsic activity and selectivity, these catalysts were shown to have a high stability over time on stream, and could easily be regenerated by means of heat treatment under air. The absence of strong acid sites, which are preferential sites for the formation of coke, could also explain the high selectivity and relative stability of these catalysts.

In the present study, we extended the analysis of ethanol and 1-butanol dehydration catalysts to include several other rare earth phosphates with the same Rhabdophane-type structure. The goal was to investigate the catalytic properties of these rare earth elements and to determine whether the conclusions concerning the reaction mechanism and the nature of most active sites on the lanthanum phosphates remained valid. La, Nd, Sm and Gd phosphates

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were thus prepared under similar conditions, and characterized and tested as catalysts for the dehydration of ethanol and 1-butanol. The acid–base properties of the catalysts were evaluated from the temperature-programmed desorption (TPD) of ammonia and CO₂ and from FTIR (Fourier transform infrared spectroscopy) analysis of several adsorbed probe-molecules (2,6 dimethylpyridine and CO₂).

2. Experimental

The rare earth phosphates were prepared as previously described [7,10]. An hydrous oxide was prepared first by dissolving commercial rare earth nitrates (0.26 mol L⁻¹) into 100 mL of equimolar water–ethanol solution containing 0.066 mol L⁻¹ of cetyltrimethylammonium bromide and about 110 mL L⁻¹ of aqueous ammonia (32 wt%). After 2 h at room temperature under stirring the resulting solid was collected by filtration, washed with distilled water and dried in air at 298 K. The solid was then digested in an aqueous solution of phosphoric acid (1 mol L⁻¹, 100 mL). The final product was filtered, washed with distilled water, dried in air at ambient temperature and calcined at 823 K for 6 h.

The Metal contents of the solids were determined by Inductively Coupled Plasma (ICP) atomic emission spectroscopy and their specific surface areas measured using the BET method with a Micromeritics ASAP 2020 instrument after degassing under vacuum at 573 K for 3 h. X-ray diffraction (XRD) patterns of the catalysts were obtained using a Bruker D5005 X-ray diffractometer using Cu K α radiation. XPS measurements were performed using a Kratos Axis Ultra DLD spectrometer. Spectra of RE 3d and 4d (RE = La, Nd, Sm and Gd), P 2p, O 1s, C 1s levels were measured using a monochromated Al K α X-ray source. Binding energies were corrected relative to the carbon 1s signal at 284.6 eV. The signal intensities of RE 4d, P 2p, O 1s and C 1s were measured using integrated areas under the detected peak.

Raman spectra were measured on a JOBIN-YVON LabRam Infinity apparatus equipped with a CCD detector operating at liquid nitrogen temperature. A D2 filter was used to protect the catalyst from destruction by the laser (wavelength $\lambda = 520$ nm). The Raman shifts were recorded in the range of 200–5500 cm⁻¹. Samples homogeneity was evaluated by performing the analyses on at least three different locations for each sample.

FTIR spectroscopy has been used to characterize the acid–base properties of the catalysts by following the spectra of adsorbed probe molecule. A Nexus 670 FTIR spectrometer equipped with a MCT or a DTGS detector was used. The phosphates were pressed into self-supporting pellets (20–30 mg, 2.01 cm²), placed in a cell, and treated at 573 K in situ under vacuum (133.32 $\times 10^{-5}$ Pa) for 1 h. They were cooled to 373 K and exposed dimethylpyridine (133.32 Pa at equilibrium) or CO₂ (13.33 Pa at equilibrium) for 15 min. The spectra (128 scans, resolution of 4 cm⁻¹, range of acquisition: 400–4000 cm⁻¹) were then recorded after evacuation under vacuum (133.32 $\times 10^{-5}$ Pa) at room temperature, 323, 373, 423, 473 and 523 K for 15 min. Spectral analyses and decompositions were carried using Omnic software. All of the spectra were normalized to a disc of 10 mg cm⁻². Temperature-programmed desorption (TPD) of NH₃ has also been used to measure the amount of acidic and basic sites and their distribution in strength. The test was done on a BELCAT thermo analyzer as previously described [11]. 60–80 mg of samples were first treated at 823 K for 1 h under helium flow (15 mL min⁻¹) to remove adsorbed species and then cooled down to 373 K before being exposed to NH₃ (or CO₂) for 30 min. Following, the system was swept by He for 15 min and temperature was programmed to increase to 823 K (8 K min⁻¹).

The dehydration of ethanol and 1-butanol was performed at atmospheric pressure as described elsewhere [7]. High purity nitrogen was used as a carrier gas and the alcohols (reagent grade) were

introduced into the carrier gas by an evaporator–saturator system. The gas mixtures passed through the catalyst packed into a glass plug-flow micro-reactor. All the pipes were heated to eliminate condensation of the alcohols and reaction products, which were analyzed online by gas chromatography. The column used was a HP plot Q with 15 m of length, 0.53 mm of diameter externally and 40 μ m of film thickness. A two-dimensional chromatography also coupled to mass spectroscopy (GC-MS-2D) of SRA instrument equipped a ZB1 column and a VF17 column, has also been used to detect traces of by-products when almost 100% selectivity to alkenes was observed. Calculated carbon balances were higher than 98%. Tests of empty reactor carried out at 628 K always showed conversion lower than 3%.

3. Results

Four rare earth phosphates (La, Nd, Sm and Gd) were prepared and studied as catalysts. Their main physical and chemical characteristics are presented in Table 1. Their specific surface areas range between 82 and 124 m² g⁻¹, whereas their pore size and volume are comparable. For all of these solids, the surface P/RE ratios derived from XPS data analysis were close to the theoretical values, except for the case of LaPO₄ (the measured value was much greater than the theoretical value). Adequate fitting of the O1s peak was systematically achieved using two components, characterized by binding energies of 531.0 and 532.7 eV, which were attributed to O²⁻ and OH⁻ surface species, respectively. The OH/(OH+O) surface ratio was comparable for all the solids, with the exception of LaPO₄, for which it was smaller.

The X-ray diffraction patterns of the solids showed a single well-crystallized Rhabdophane-type phase only, for all of the prepared samples (ICSD 046-1439). The Rhabdophane structure crystallized in the hexagonal system with space group P6₂22 [12]. The computed *a* and *c* unit cell parameters of the phosphates are provided in Fig. 1, showing that they vary almost linearly with the crystal ionic radii of the eight-coordinated lanthanide cations [13]. A similar effect, due to lanthanide contraction, has been previously demonstrated [14]. The thermal and thermo-gravimetric analyses of lanthanide phosphates under air showed that they were hydrated, and that dehydration, corresponding to approximately 1 mole of water per mole of phosphate, systematically occurred in two phases between 298 K and 563 K. The first mass loss was attributed to absorbed water, whereas the second (0.3–0.4 mol) was attributed to water molecules located in the channels of the structure. The departure of the latter water molecules took place in only one step, and did not lead to the collapse of the structure. These results are also in good agreement with those previously reported

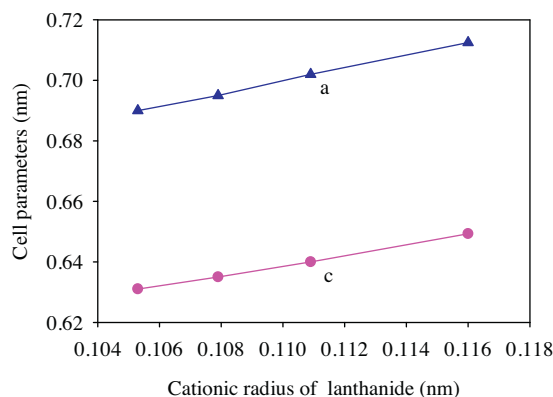


Fig. 1. Variation of the unit cell parameters of the phosphate with Rhabdophane structure as a function of the cationic radius of the lanthanide elements [6].

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