



Ti(III)APO-5 materials as selective catalysts for the allylic oxidation of cyclohexene: Effect of Ti source and Ti content



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ARTICLE INFO

Article history:

Received 22 July 2013

Received in revised form

19 September 2013

Accepted 20 September 2013

Available online 25 October 2013

Keywords:

TAPO-5

Ti(III)APO-5

Cyclohexene oxidation

Allylic oxidation

Ti(III) source

2-Cyclohexenyl hydroperoxide

ABSTRACT

Different TAPO-5 materials, prepared from Ti(III) chloride, have been tested as catalysts in the oxidation of cyclohexene with hydrogen peroxide under anhydrous conditions. Solid TiCl_3 was shown to render better synthesis reproducibility and higher catalytic activity of the resultant materials compared to TiCl_3 aqueous solution. The synthesis of these materials was carried out under N_2 atmosphere to preserve the initial oxidation state of Ti during the crystallization process. As a consequence, the so-called Ti(III)APO-5 materials have Ti environments different to those found in conventional TAPO-5 (Ti(IV)APO-5). Indeed, their catalytic activity in the oxidation of cyclohexene markedly overcomes that of the Ti(IV)APO-5 at any Ti content and after any reaction time. Turnover number (TON) of Ti(III)APO-5 samples exponentially increases as Ti content decreases, the Ti-poorer sample (Ti/(Ti + Al + P) molar ratio of 0.003) reaching TON values higher than 200 after 6 h of reaction at 343 K and higher than 550 after 24 h. The interest of Ti(III)APO-5 catalysts lies on their high selectivity to products formed through allylic oxidation of cyclohexene. The main product of this reaction, 2-cyclohexenyl hydroperoxide, was obtained with more than 80% selectivity over Ti(III)APO-5 catalysts. This behavior is in contrast with the well-known strong tendency of the more active Ti-zeolites to epoxidize the double bond.

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1. Introduction

Since the discovery in the early eighties of the ability of TS-1 to catalyze the selective oxidation of organic compounds [1], the application of Ti-zeolites as heterogeneous catalysts for the oxidation of organic substrates under mild conditions has been the subject of a large number of studies [2–5]. The interest in this kind of zeolitic materials led to explore other potential Ti-containing materials, such as silica-based mesoporous ones, which would allow processing larger molecules [6–8]. However, in contrast to the continuous development of highly active Ti-zeolites and Ti-mesoporous materials, the attempts carried out with the related group of titanium-doped AlPO_4 -based microporous zeotypes have failed to render interesting catalysts. In spite of the large number of the so-called TAPO materials with different structures that have been prepared [9–11], up to date, their catalytic performance in those oxidation processes [12–15] has been shown poor compared to that of Ti-zeolites.

Several aspects that make TAPOs different to Ti-zeolites have to be considered in order to develop strategies to enhance their

catalytic performance. First, both networks are inherently different in hydrophobic/hydrophilic terms, in such a way that the more hydrophilic AlPO_4 framework favors the selective adsorption of the most polar molecules. The influence of hydrophobicity/hydrophilicity on the catalytic activity has been already made clear in Ti-zeolites by modifying the polarity of their frameworks or the reaction conditions [4,15–18]. A second difference between TAPOs and Ti-zeolites is the Ti environment obtained by the isomorphous substitution of tetrahedral atoms in both materials. When Ti(IV) ions are introduced in zeolitic frameworks, they can only substitute isoelectronic Si(IV) atoms, necessarily leading to $\text{Ti}(\text{OSi})_4$ environments. However, Ti(IV) replaces more likely P(V) atoms in an AlPO_4 framework, generating $\text{Ti}(\text{OAl})_4$ environments. Such environments are thought to inhibit the activity of Ti centers as deduced from the lower catalytic activity of Ti-zeolites containing aluminum compared with their Al-free analogues [4,19]. Recently, Chiesa and co-workers [20–22] have reported some spectroscopic studies indicating that Ti(IV) in an AlPO_4 material can also be incorporated by pairs, so that two Ti atoms replace a P(V) atom and its contiguous Al(III) generating Ti–O–Ti units, just like Si(IV) can do in the case of SAPO materials [23,24]. Moreover, though isolated titanium centers in P(V) positions and/or Ti–O–Ti pairs are found in the material, titanium atoms in aluminum sites have been proven to play the most important role for redox catalytic activity [22].

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Recently, we have presented some innovative strategies in TAPO-5 synthesis [25,26], which take advantage of the higher versatility of AlPO_4 frameworks compared to zeolite ones to incorporate heteroatom ions with different charges. Such versatility would, in principle, allow to change the Ti environment within the aluminophosphate framework by means of its incorporation as Ti(III). This cation would occupy preferably Al(III) sites in order to maintain the charge balance of the framework, and would give rise to $\text{Ti}(\text{OP})_4$ environments. In addition, the presence of Ti–O–Ti pairs would be prevented since replacing contiguous P(V) and Al(III) by two Ti(III) ions would entail an excessive negative charge in the framework, hardly compensated by a mono-protonable amine, which is the most common structure directing agent in AIPs.

We have reported elsewhere that this approach indeed generates TAPO-5 catalysts that are more active than the conventional ones, being able to oxidize cyclohexene at a rate of the same order as large-pore Ti-beta [27] under suitable conditions. This work extends the study of TAPO-5 materials prepared from gels containing Ti(III) ions, here called Ti(III)APO-5, as catalysts in the cyclohexene oxidation with H_2O_2 under anhydrous conditions. The influence that Ti content in Ti(III)APO-5 materials has on the intrinsic activity of Ti centers has been also investigated, discussed, and critically compared with the conventional TAPO-5 catalysts prepared using Ti(IV) sources.

2. Experimental

2.1. Catalysts preparation

Ti(III)APO-5 samples were prepared with different titanium content by hydrothermal treatment using titanium trichloride as Ti(III) source [25,26], in one of these two formulations: (i) as TiCl_3 (~10 wt%) in HCl (20–30 wt%) aqueous solution (supplied by Aldrich with the exact composition), and (ii) TiCl_3 powder (Aldrich). The general gel composition was $(1-x)\text{Al}:1.0\text{P}:x\text{Ti(III)}:m\text{MCHA}:25\text{H}_2\text{O}:n\text{HCl}$ for the former TiCl_3 source, where x denotes the Ti/P molar ratio, n is the HCl/P molar ratio resultant after its inevitable addition with TiCl_3 in hydrochloric acid solution, MCHA refers to N-methyldicyclohexylamine and m designates the MCHA/P molar ratio, which was varied to compensate the changes of pH introduced by the HCl added, so that the pH value of the gel was forced to be in the range 6.5–7.0. When the TiCl_3 powder was used, the gel composition was simplified to $(1-x)\text{Al}:1.0\text{P}:x\text{Ti(III)}:0.8\text{MCHA}:25\text{H}_2\text{O}$ having pH values in the same range. Both the preparation of the gel and the following autoclaves sealing were carried out under inert atmosphere, in a glove bag filled with nitrogen. The TiCl_3 source was added over an aqueous solution of phosphoric acid (85 wt%, Sigma) in deionized water, which turns into purple color. Next, $\text{Al}(\text{OH})_3 \cdot x\text{H}_2\text{O}$ (Sigma–Aldrich) was added over the solution and the resultant suspension was vigorously stirred for ca. 10 min, followed by the dropwise addition of N-methyldicyclohexylamine (MCHA). This amine was selected as structure directing agent (SDA) because of its high specificity to AFI-structured AlPO_4 -based materials [28]. In particular, this specificity has already been proven for AlPO_4 materials doped with the same heteroatom, Sn, in two different oxidation states [29]. The resultant gel was stirred for 1 h before transferring it into Teflon-lined stainless steel autoclaves for the hydrothermal treatment at 448 K under autogeneous pressure. The obtained purple solids, whose color indicated that at least part of the Ti present in the solid maintains its oxidation state 3+ after the crystallization process, were recovered by filtration and washed with deionized water. After drying under ambient atmosphere, the solids became yellowish white, suggesting that Ti(III) was oxidized to the most stable titanium oxidation state, Ti(IV).

Conventional Ti(IV)APO-5 catalysts were prepared strictly following the procedure described elsewhere [30], with the molar gel composition $1.0\text{Al}:1.0\text{P}:x\text{Ti(IV)}:0.5\text{TPOAH}:20\text{H}_2\text{O}$, using titanium isopropoxide (Aldrich) as Ti(IV) source.

The samples prepared with Ti(III) sources will be named as Ti(III)APO-5, while Ti(IV)APO-5 will denote the conventional samples prepared with the Ti(IV). The general term TAPO-5 will be used to refer to both Ti(III)APO-5 and Ti(IV)APO-5 materials. The nomenclature used for every particular solid will be as follows: the oxidation state of titanium source, followed by a letter only in the case of Ti(III)APO-5 samples to indicate the type of TiCl_3 source used ('p' for powder and 's' for solution), next a number that will indicate the titanium/phosphorous percent molar ratio in the gel ($\times 100$ times) and finally the crystallization time will be indicated by the number of hours (h) or days (d). As an example, Ti(III)p-1-4h will then denote the sample prepared with TiCl_3 powder, with a titanium content in the gel $x=0.01$ and after 4 h of crystallization.

Prior to catalytic tests, all TAPO-5 samples were calcined, in order to eliminate the SDA molecules. The solid samples were heated under a N_2 flow of 100 mL min^{-1} from room temperature to 823 K (at a heating rate of 3 K min^{-1}) and kept at this temperature for 1 h. Then they were maintained under an airflow of 100 mL min^{-1} at 823 K for 5 h. Complete removal of the organic molecules was certified by thermogravimetric analysis.

2.2. Characterization techniques

Nature and purity of crystalline phases were studied by powder X-ray diffraction (PXRD) using a PANalytical X'Pert Pro diffractometer (Cu $\text{K}\alpha$ radiation). Diffuse reflectance UV-visible (DRUV) spectra were recorded with a Cary 5000 Varian spectrophotometer equipped with an integrating sphere using the synthetic polymer Spectralon as reference. The spectra were corrected applying the Kubelka–Munk function. The chemical composition of the solids was determined by inductively coupled plasma (ICP-OES) spectrometry with an ICP Winlab Optima 3300 DV Perkin–Elmer spectrometer. Scanning electron microscopy (SEM) micrographs were taken in a FEI Nova NANOSEM microscope with a vCD detector. Nitrogen adsorption/desorption isotherms were measured at 77 K in a Micromeritics ASAP 2010 equipment. Calcined samples were previously degassed at 623 K for 16 h. Surface areas were estimated by applying the BET method, and micropore volume was obtained by application of the t -plot method to the N_2 adsorption data.

2.3. Catalytic experiments

Catalysts were tested in the oxidation of cyclohexene with H_2O_2 under anhydrous conditions as described elsewhere [27]. These conditions were reached after removing almost all the water that accompanies the commercial 30 wt% H_2O_2 aqueous solution. Water was removed by Soxhlet extraction of solutions prepared dissolving the 30 wt% H_2O_2 solution in acetonitrile. The reactions were carried out in batch mode using a round bottom flask equipped with a magnetic stirrer, a thermometer and a covered reflux condenser provided with a drying tube on top. The later was used in order to avoid the condensation of ambient humidity inside the condenser caused by the low temperature of water circulating through it. The coolant water temperature was controlled at 278 K to prevent any evaporation of the chemicals during the reaction. Calcined catalysts were activated overnight inside the reaction system at 433 K under a flow of N_2 to remove any water adsorbed into the catalyst channels. Under the reaction conditions used, mass balance was ca. 98% after 30 h of reaction.

In a typical experiment, 3.0 g of cyclohexene, the corresponding amount of H_2O_2 in CH_3CN solution (previously submitted to

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