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Enhanced catalytic activity of TAPO-5 in the oxidation of cyclohexene with hydrogen peroxide under anhydrous conditions

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This work studies the influence of the amount of water accompanying and stabilizing the conventional oxidant agent H_2O_2 on the activity of different TAPO-5 materials in cyclohexene oxidation, in comparison to that of the par excellence large-pore Al-free Ti-beta zeolite. It was proved that the catalytic activity of a TAPO-5 markedly and systematically increases as the amount of the oxidant H_2O_2 (30 wt.% in aqueous solution) decreases, suggesting the strong inhibitor role of water in the catalytic activity of TAPOs. Following this noteworthy result, we have developed a method for removing water from the mixture solvent (acetonitrile)/H_2O_2 30 wt.% (aqueous solution) based on a Soxhlet extraction. Water content was quantified by FTIR, which certified the reproducible reaching of a nearly anhydrous system (5 mg H_2O/g CH_3CN). Under these conditions, TAPO-5 catalysts were able to convert cyclohexene in an extension higher that half of that given by Ti-beta. The product selectivity given by TAPOs and Ti-beta is completely different, as the former favors the cyclohexene reaction through radicalary mechanism and Ti-beta almost exclusively gives epoxidation products. The catalytic features of the conventional Ti(IV)APO-5 is improved by the new so-called Ti(III)APO-5 catalyst, synthesized from gels containing Ti(III).

1. Introduction

The incorporation of Ti ions into zeolite frameworks [1] allowed microporous materials to extend their applications as heterogeneous catalysts to redox processes under mild conditions [2]. Along the time, potential and/or real industrial applications of Ti-zeolites [3,4] and Ti-containing silica-based mesoporous materials [5] in the field of Fine Chemistry have continued increasing. These catalysts are able to efficiently catalyze a large number of oxidation reactions, providing the added value of the shape-selectivity [2–4]. That success has not been shared by their homologue $AlPO_4$-based microporous materials, in spite of Ti incorporation into the $AlPO_4$ framework is out of any doubt [6–8]. Interestingly, its homologue Fe or Mn-doped $AlPO_4$-5 materials have been shown as active in oxidation reactions under similar conditions to those used for Ti-zeolite catalysts [9]. This uneven behavior between the different Ti-containing microporous materials as a function of the framework composition can be attributed to diverse causes: (a) the different Ti environment [10,11], $Ti(OSi)_4$ being particularly favorable; (b) the higher hydrophilic character [11,12] of $AlPO_4$ framework in contrast to the hydrophobic nature of all-SiO_2-based materials [13,14]; or (c) the undesired (for redox catalytic purposes) acidity [10,12] associated to the most accepted Ti^{4+} ion incorporation in P^{5+} sites of an $AlPO_4$ framework [15], in contrast to the charge balance arising from the Ti^{4+} ions incorporation occupying isoelectronic Si^{4+} sites. The lower activity of more hydrophilic and acidic Al-containing Ti-beta against its Al-free homologue zeolite [10,12] does not conclusively resolve anything in this sense, as it could be due to the reasons (a), (b) and/or (c). Similarly, Ti-MCM-41 was not able to reach the catalytic conversions of Ti-zeolites when the latter have no diffusional problems [5,16]; it is also different from a Ti-zeolite in Ti environment (but not in the siliceous nature of their first coordination sphere) and in its hydrophilicity due to its abundant silanols. In any case, all these results suggest that the Ti environment is probably not the only factor that accounts for the catalytic features of the material in which it is incorporated. Therefore, it is likely that the low activity of TAPOs is susceptible of being improved by, for instance, modifying the hydrophilicity of the catalytic reaction media. In this sense, outstanding differences in activity have been found by simply changing different reaction conditions, such as reactants electrophilicity [10] or solvent nature [17]. Even removal of water from reaction liquid medium, which is one of the subjects of this work, has been reported to improve the catalytic activity of Ti-MCM-41 catalysts [18].

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The number of publications about TAPOs as catalysts in oxidation reactions is rather scarce [13,19–21]. It is surprising that, chronologically speaking, the first publication of them is not about a proper TAPO catalyst but about Ti-containing SAPO-5 catalyst (the so-called TAPSO-5 [13]) attempting to imitate the siliceous Ti environment of Ti-zeolites. The TAPSO approach in principle means the reduction at some extent of every above-mentioned possible sources of the low activity of TAPOs, as it would make more siliceous the Ti environment, increase the hydrophobic character of its framework, and decrease the acidity directly associated to the Ti incorporation in P sites. Unfortunately, that study was not able to shed light on the ultimate cause responsible of the low catalytic activity of TAPOs as TAPSO activity was not compared to that of any of the two pertinent catalysts: its homologue Si-free TAPO-5 and a Ti-zeolite of a similar pore openings (large pore defined by 12-membered rings). The same is applicable for the study of catalytic activity of Ti-substituted SAPO-5 and Si-VPI-5 tested in phenol hydroxylation [20].

Recently, the combination of different advanced characterization techniques applied to the study of Ti environments in TAPOs has renewed the interest for these materials [7,8,22]. It has been suggested that, unlike Ti^{4+} incorporation in Ti-zeolites but just like Si^{4+} incorporation in an $AlPO_4$ framework, Ti^{4+} ions have different incorporation mechanisms including that by pairs (known as mechanism SIII in SAPO materials [23]), which implies the existence of Ti—O—Ti bonds into the framework of the conventional TAPO materials.

We have been developing a research project aimed to contribute to the knowledge behind the much lower catalytic activity of the conventional TAPOs against Ti-zeolites, and accordingly to design strategies to make TAPOs competitive oxidation catalysts. Our approaches are based on the rational design of both new Ti environments in the catalyst and of the reaction conditions. The generation of new Ti environments in AlPOs as well as their catalytic implications is deeply discussed elsewhere [24,25], and a typical catalyst resultant of applying that strategy is also used in the current article (denoted as Ti(III)APO-5), which has been prepared from gels containing Ti(III) ions instead of the conventional Ti(IV) ones. This work focuses on the effect of reaction conditions, particularly water content of the oxidant agent H_2O_2 and reaction media, on the catalytic behavior of both conventional TAPO-5 and the so-called Ti(III)APO-5. This study presents some singularities respect to the previous publication studying the effect of water removal in the activity of Ti-MCM-41 in similar reactions but using as-received 'anhydrous' TBHP [18]: the magnitude of water to remove is much higher in our case, H_2O_2 decomposes in direct contact to the Molecular Sieve, and the characterization technique used in ref. 18, ^1H NMR, has intrinsic limitations for quantifying H_2O and H_2O_2 from a mixture solution [26].

2. Experimental

2.1. Catalysts preparation and characterization

Ti(III)APO-5 sample was synthesized [24,25] by hydrothermal treatment of a gel with the following molar composition: 0.96 Al:1.0 P:0.04 Ti(III):0.8 MCHA:25 H_2O. Both the preparation of the gel and the subsequent autoclave sealing were carried out under N_2 atmosphere. In a typical gel preparation, $TiCl_3$ aqueous solution (~10 wt.%) in HCl (20–30 wt.%) (supplied by Aldrich with the exact composition) was added over a solution of phosphoric acid (85%, Aldrich) in deionized water turning it into deep purple color. Next, $Al(OH)_3 \cdot xH_2O$ (Sigma) and straightaway the organic structure directing agent (SDA) N-methyldicyclohexylamine (MCHA) were added under vigorous stirring. The resulting mixture was stirred for one hour and the final gel was introduced in Teflon-lined stainless-steel autoclaves and subsequently hydrothermally treated at 448 K under autogeneous pressure for 18 h. The resultant purple solid, whose color indicated that at least part of Ti present in the solid maintain its oxidation state 3+ after crystallization process, was recovered by filtration and was washed with deionized water. Once dried, the solid became yellowish white, due to the complete oxidation of Ti to its oxidation state 4+.

Conventional catalysts, Ti(IV)APO-5 and Ti-beta, were prepared strictly following the procedures described elsewhere [27,28] with Ti content either having showed high catalytic activity [27] or specifically designed to have a Ti content similar to that of Ti(III)APO-5, respectively. In order to clarify the differences between the samples Ti(III)APO-5 and Ti(IV)APO-5, a detailed description of the synthesis procedure for preparing Ti(IV)APO-5 is also described next. Ti(IV)APO-5 was prepared from a gel with a molar composition of 1.0 Al:1.0 P:0.02 Ti (IV):0.5 TPAOH:20 H_2O, using titanium tetraisopropoxide as Ti source. First, pseuboehmite (Catapal B 73.56 wt.% Al_2O_3) was added over an aqueous solution of phosphoric acid (85%, Aldrich) in deionized water. Then, titanium isopropoxide (Aldrich) and subsequent TPAOH as SDA were added dropwise. After 1 h of vigorous stirring, the homogeneous gel was transferred into a Teflon-lined stainless-steel autoclave, which were hydrothermally treated at 175 °C for 192 h.

The most extended nomenclature for denoting the here-called Ti(IV)APO-5 is TAPO-5 (sometimes, TiAPO-5). However, in this article, we will use the term TAPO-5 to encompass both Ti(III)APO-5 and Ti(IV)APO-5. The final composition of the inorganic frameworks as determined by ICP analyses were: $Ti_{0.026}Al_{0.497}P_{0.477}O_2$ for Ti(III)APO-5, $Ti_{0.007}Al_{0.521}P_{0.473}O_2$ for Ti(IV)APO-5 and $Ti_{0.017}Si_{0.983}O_2$ for Ti-beta.

Before catalytic tests SDA molecules were eliminated from all the samples by calcination at 823 K for 5 h under an air flow of 100 mL min^{-1}. Previously the samples had been heated at a rate of 3 K min^{-1} under a N_2 flow of 100 mL min^{-1} up to 823 K and maintained at this temperature for 1 h under these same conditions.

The nature of crystalline phases was determined by powder X-ray diffraction (PXRD) patterns, collected by a PANalytical X'Pert Pro diffractometer using Cu Kα radiation. UV–visible diffuse reflectance spectra were registered on a Cary 5000 Varian spectrophotometer equipped with an integrating sphere and the obtained data were converted to corresponding spectra expressed according to Kubelka–Munk function.

2.2. Water extraction from acetonitrile–H_2O_2 30 wt.% mixture. Quantification of H_2O and H_2O_2

Some catalytic experiments were carried out over an acetonitrile–H_2O_2 30 wt.% mixture, after water extraction in a Soxhlet system. Molecular Sieve 3A was used as adsorbent selective to water, being able to discriminate between that small molecule and the more volatile CH_3CN and less volatile H_2O_2 ones. To perform the experiment, 30 g of Molecular Sieve, previously dehydrated at 453 K, were wrapped within a filter paper bag and placed in the Soxhlet thimble whereas a mixture solution of CH_3CN and H_2O_2 30 wt.% aqueous solution in a proportion of 30 mmol of H_2O_2 per mol of CH_3CN was put into the still pot. (Due to the risks of heating concentrated hydrogen peroxide, especially in the presence of organic compounds, it is not recommendable to carry out this experiment in absence of acetonitrile or with low acetonitrile/H_2O_2 ratio). The amount of Molecular Sieve 3A was chosen supposing a theoretical water adsorption capacity of 15 wt.% (real adsorption of ~20 wt.%). The mixture was heated up to 349 K under magnetic stirring. Small aliquots were taken out from the still pot after every Soxhlet extraction cycle and they were analyzed by FTIR in order to quantify H_2O_2 and the remaining amount of water until a