One step-synthesis of highly dispersed iron species into silica for propylene epoxidation with dioxygen

J. García-Aguilar [a], I. Miguel-García [a], J. Juan-Juan [b], I. Such-Basáñez [b], E. San Fabián [c], D. Cazorla-Amorós [a], Á. Berenguer-Murcia [a,*]

[a] Materials Science Institute and Inorganic Chemistry Department, Alicante University, Ap. 99, E-03080 Alicante, Spain
[b] Research Technical Services, Alicante University, Ap. 99, E-03080 Alicante, Spain
[c] Materials Science Institute and Physical Chemistry Department, Alicante University, Ap. 99, E-03080 Alicante, Spain

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ABSTRACT

Well dispersed iron catalysts were synthesized in silica ($Fe_{0.0x}SiO_2$) by a one-step synthesis procedure. These materials were tested in the propylene epoxidation reaction with gaseous O_2. The influence of the iron metal loading on the iron incorporation and distribution in the support (both influenced by the synthetic procedure) were thoroughly studied (conversion, generation and selectivity). Electron Microscopy and UltraViolet–Visible (UV–VIS), Raman and Fourier Transform Infrared Spectroscopy (FTIR) spectroscopy techniques were used to analyze the iron distribution in the catalysts and to probe its incorporation into the silica framework. In situ FTIR was also used to analyze the interaction between propylene and iron-based catalysts. Computational calculations considering a single-site iron catalyst incorporated into the silica structure show a possible interaction between O_2 and the incorporated iron atom and the olefin bond and the acidic proton neighboring the iron species which favor the reaction between the two molecules near the iron atom.

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1. Introduction

In the last years, the fine chemical industry is facing an important challenge concerning the production of one important intermediate in the synthesis of polyurethanes, cosmetics, solvents, detergents and other relevant products. This new attractive compound is propylene oxide (PO) and its properties and reactivity make this product one of the most widely studied, not only by academic researchers, but also by the main chemical manufacturers, such as DOW Chemical and LyondellBasell Industries [1]. PO is principally consumed in the production of polyether polyols for urethanes (65%) and the synthesis of propylene glycols (19%) and glycol ethers (6%), these compounds being synthesized by oligomerization, hydration and alcoholysis of raw PO, respectively [2].

In the industrial scale synthesis of PO, propylene is used as raw material. In this sense, approximately 7% of the world consumption of propylene is for PO production, representing the third product generated from this precursor, only behind polypropylene (62%) and acrylonitrile (8%) [2]. Nowadays, the main PO production route is the liquid-phase reaction, known as chlorohydrin process, with

approximately 50% of PO production. Other liquid-phase PO production processes employed in industry nowadays include the styrene co-product process (33% PO production worldwide), the tert-butyl co-product process (15%), the HPPO (hydrogen peroxide-based) process (5%), and the Sumitomo cumene-based process (5%). Some problems associated with these syntheses are the use of chlorine and sub-production of chlorinated organic compounds in the reaction that result in a complicated separation and purification of PO [3].

In this sense, propylene epoxidation to propylene oxide by gas–solid phase heterogeneous catalysis could avoid the use of hazardous oxidation agents such as Cl_2, in the liquid phase and replace them with other safer compounds, such as H_2/O_2 mixtures or O_2 in the best-case scenario [2,4]. In the literature, the most common and widely developed catalysts for this process are based in titano-silicate supports (Ti–SiO_2) with well dispersed Au nanoparticles on the surface of the material. This kind of materials presents very well dispersed Ti(IV) species on the silica matrix, generally with low Ti/Si ratios. In these cases, the chemical properties of the Ti–SiO_2 reflect in an enhanced performance of the active phase in the epoxidation process compared to the behavior of pure TiO_2-based catalysts, in terms of both activity and selectivity for the process [5,6].

Moreover, the deposition of low metal loadings of Au as nanoparticles (less than 5 nm in size) drastically increases the selectivity (over 90% toward PO) at temperatures above 100–200 °C. These catalysts have been widely studied and nowadays the reaction mechanism for this active phase is well known, with the formation of hydroperoxo and peroxo species on the metal nanoparticles and their interaction with propylene molecules adsorbed on titanium sites [7] being responsible for the high selectivity toward PO.

These catalysts have been developed in microreactor configurations [8] and membrane reactors [9]. However, the use of H_2/O_2 mixtures in the gas stream is mandatory to achieve an acceptable selectivity toward PO. In this sense, many works have demonstrated the validation of these supports, by modifying the silica support, the titanium precursor and the Au nanoparticles deposition method. Nevertheless, some aspects such as low propylene conversion, water formation and the low H_2 efficiency are the main drawbacks of this active phase and still need to be overcome. Recently, some authors have tested this kind of gold-based catalysts (Au/TiO_2) in a different oxidative atmosphere (CO/O_2) with comparable results (in terms of propylene conversion and PO selectivity) to those reached under a H_2/O_2 gas stream composition [10]. Ag nanoparticles have been also supported on TiO_2, but poorer results have been obtained compared to the gold-based catalysts, yielding lower propylene conversions [11]. Also, similar catalysts such as $Ti–SiO_2$ loaded with Pt or Pd nanoparticles have been tested in the epoxidation of propylene in liquid phase by in situ generation of H_2O_2 adding H_2 and O_2 in the organic phase [12].

On the other hand, the use of a gas stream with O_2 as oxidative agent, without the addition of H_2, is employed in some catalysts for the synthesis of PO by epoxidation of propylene. Ag-based catalysts on different supports (such as $CaCO_3$, Al_2O_3, MoO_3/ZrO_2 and WO_3) [3,13], have been studied in the epoxidation of propylene with O_2 between 250 and 350 °C. The catalytic behavior of these materials shows lower selectivity than the $Au/Ti–SiO_2$ systems in H_2/O_2 gas stream compositions but with a similar propylene conversion [14]. In other related works, the catalysts studied for the propylene epoxidation reaction are based on different metal oxides (Ru and/or Cu) [15–17] also tested in O_2-containing atmospheres. In these cases, a PO selectivity of 35% and 9% propylene conversion is achieved for a 2% Cu-5% Ru-1.75% NaCl promoted catalyst supported over silica at 350 °C. Also, mixed copper/manganese oxides promoted with NaCl at 300 °C, have displayed propylene conversions around 5% and PO selectivities of 25% [18]. Other works use more complicated systems to achieve good catalytic behaviors, such as $Ti–MoO_3–Bi_2SiO_5/SiO_2$, that display 20% of propylene conversion and 60% of PO selectivity at 500 °C [19].

Some works have studied iron impregnated or incorporated in silica as active phase for selective hydrocarbon oxidations. In this sense, the iron location (framework or extra-framework), iron coordination (tetrahedral or octahedral) or its distribution (single-sites, clusters or small particles) are the main factors discussed for the selective oxidation but, in all cases, the iron has been stated to produce the decomposition of the oxidizing agent (H_2O_2 or N_2O) and the resulting adsorbed atomic oxygen has been identified as the species responsible for the oxidation. As an example, the activation of N_2O for the oxidation of benzene to phenol requires extra-framework iron species in Fe–MFI catalyst [20]. In the epoxidation of styrene with H_2O_2, two different species of iron have been found to be important for the oxidation reaction, i.e., iron oxide clusters are responsible for the H_2O_2 decomposition and tetrahedral iron in framework positions are the sites where the epoxidation effectively takes place [21]. This kind of well-dispersed iron-based catalysts has been also used for selective oxidations in other liquid phase processes, with very successful results [22,23].

In the propylene epoxidation reaction using iron-based catalysts, the use of a more oxidant compound, such as N_2O at 350 °C, is necessary for the PO synthesis in the gas-phase reaction [24–27]. Ananieva et al. studied the effect of Na^+ and Cs^+ in the acidity of the support to decrease the possibility of PO polymerization [24]. In addition, Horváth et al. focused their work on the addition of the alkaline promotor K^+ (as KCl) in order to enhance the catalytic properties of the iron containing catalyst. Maximum PO selectivity during the catalytic tests was achieved (around 75%) for a KCl promoted iron impregnated silica, but deactivation of the catalyst was observed due to carbon deposition on the catalyst, even when the promoting agent was added. In this sense, the authors propose that the epoxidation reaction takes place *via* the oxygen-atoms abstracted from the N_2O which decomposes in the medium. The specific iron species responsible for the N_2O decomposition could transfer the oxygen atoms and react with propylene, generating PO [25]. Most of these related, promoted or unpromoted, catalysts used in propylene epoxidation reaction have been prepared using multiple-step procedures (e.g. support preparation and/or metal impregnation).

In this work, we present a one-step synthesis method for the preparation of Fe–SiO_2 catalysts, with very well dispersed iron species into the silica structure, and their application in the propylene epoxidation reaction using only the O_2 molecule as oxidant. The comparison between samples with different preparation procedures (one-step synthesis and impregnation) and their characterization by different spectroscopic (UV–VIS, Raman and FTIR), microscopy (TEM and FE-SEM) techniques and complementary simulation calculations (dispersion-corrected DFT) allows obtaining information about the reaction mechanism for the epoxidation reaction investigated on the postulated iron species incorporated into the silica structure.

2. Experimental

2.1. Catalyst preparation

2.1.1. Preparation of the $Fe_{0.0X}SiO_2$ catalysts (one-step synthesis)

The mesoporous Fe-doped silica catalysts have been prepared adapting a sol–gel synthetic protocol described for pure SiO_2 in other works [28,29].

In a typical synthesis, 0.400 g of surfactant (Pluronic® F127, BASF), 0.452 g of urea (Sigma-Aldrich) and 5.052 g of 0.01 M acetic acid solution were mixed under vigorous stirring for 80 min, the final pH of the resulting solution being around 4. Then, the necessary amount of iron precursor (iron (III) nitrate nonahydrate, Fe$(NO_3)_3$·$9H_2O$, 99.99%, Sigma-Aldrich) is added in the solution and the mixture is stirred for 1 h. Subsequently, the solution was cooled in an ice-water bath maintaining the stirring and the silica precursor was added dropwise (2.030 g Tetramethyl orthosilicate, TMOS, Sigma-Aldrich). This solution was kept under stirring for 40 min at 0 °C.

Finally, the sol was introduced in a Teflon autoclave and heated at 40 °C for 20 h to produce the aging of the sol (the pH after this step remained around 4). After this, the sample is submitted to a hydrothermal treatment at 120 °C for 6 h, to produce the urea decomposition (the final pH of the supernatant liquid being around 9–10). After this step, a dark supernatant liquid phase is observed for samples with a Fe/Si ratio over 0.01, which was removed from the top of the monolith generated, corresponding to the excess of Fe not incorporated in the SiO_2 structure. As a final step, the monolith is calcined at 550 °C for 6 h to eliminate the surfactant and the rest of unwanted precursors.

Four samples with different Fe/Si molar ratios have been prepared (namely 0.005, 0.01, 0.02 and 0.03). Higher Fe content