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Effect of Ti Speciation on Catalytic Performance of TS-1 in the Hydrogen Peroxide to Propylene Oxide Reaction

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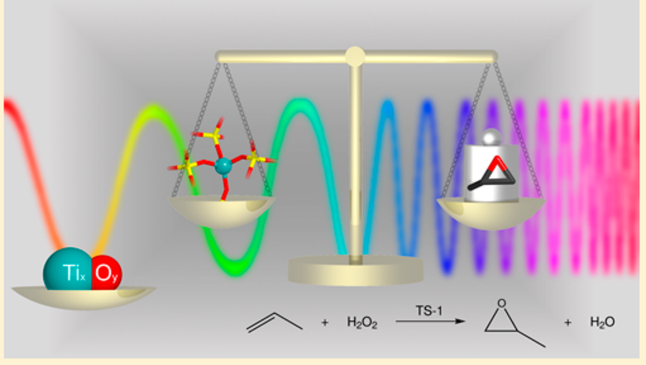
Supporting Information

ABSTRACT: Hydrogen peroxide to propylene oxide (HPPO) reaction is an attractive process exploiting titanium silicalite-1 (TS-1) as a catalyst in combination with aqueous hydrogen peroxide as an oxidizing agent. Beyond the industrial interest, TS-1 represents one of the most widely characterized catalysts due to its unique properties. However, a unified description on the speciation of the different Ti species and their correlation to catalytic performances is missing in the literature. This work aims to exploit spectroscopic techniques (namely, diffuse reflectance UV−vis, Raman, FT-IR, and Ti K-edge XANES) in a qualitative and quantitative way to thoroughly characterize Ti sites in a selected set of industrially relevant TS-1 samples, each one owning a peculiar Ti speciation. The outcomes of this study have been then related to the activity of each catalyst in HPPO reaction, showing its linear correlation with the content of perfect Ti sites (i.e., isomorphously substituting Si in the zeolitic framework). Other Ti species, such as amorphous TiO_x and bulk titania, are instead not involved in the peroxide conversion (neither in a detrimental way).



1. INTRODUCTION

Titanium silicalite-1 (TS-1), a synthetic zeotype where titanium atoms are introduced as isomorphous substituents of the tetrahedral silicon sites in a purely siliceous MFI zeolite,[1] is an important selective catalyst in low-temperature partial oxidation reactions. Being used in combination with aqueous solutions of hydrogen peroxide, TS-1 is able to catalyze selective oxidation reactions for a large variety of organic substrates with minimal byproduct production, such as the epoxidation of alkenes[2−11] and other allylic/aromatic compounds (alcohols, aldehydes, ketones).[12−20] Among these, the conversion of propylene to propylene oxide through the hydrogen peroxide to propylene oxide (HPPO) reaction[4−6,10] is one of the most investigated processes as it is an economically and ecologically superior technology since, potentially, water is the only waste product.[21] The industrial process (as independently developed by Evonik/Uhde and BASF/Dow Chemical) exploits fixed-bed reactors operating in continuous flow conditions.[6]

Even though plain TS-1, as originally synthesized by its inventors, already exhibits high performances in partial oxidations, along the years many academic and industrial studies have attempted to further improve it. Excluding improvements related to the process and reaction conditions (indeed falling outside the focus of this work), two fundamental research lines mainly dealt with the increase of TS-1 performances: (i) the improvement of the microporous TS-1 transport properties by inducing additional porosities and/or peculiar morphologies and (ii) the final elucidation of the catalytic role of the possible Ti species present in TS-1 to tune the syntheses in order to favor the formation of the most active ones.

The introduction of meso- and/or macroporosities in the microporous network of a plain TS-1 ensures the enhancement of the catalytic properties, mainly due to the overall improvement of the catalyst transport properties.[22−35] Another route to achieve similar results is to shorten the diffusion path along the microporous system by decreasing the size of the TS-1 crystals.[36−38]

Concerning the study of the different Ti species, in the last decades the research topic was mostly focused on the characterization, with both experimental[8,39−48] and computa-

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