

The type of defects in Ti-zeolites and their role in catalysis: EXAFS and XANES study

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Introduction

Titanium Silicalite-1 (TS-1) is a synthetic zeolite where Ti atoms are introduced as isomorphous substituent of tetrahedral Si sites in a purely siliceous MFI zeolite [Bordiga et al. *Phys. Chem. Chem. Phys.*, **2007**, 9, 4854]. TS-1 represents the prototype of a single catalyst due to its crystalline structure and its well-defined Ti sites. Whereas past investigation focused on perfect tetrahedral Ti (TS-1a), nowadays the focus is progressively moving toward the characterization of non-perfect Ti species (TS-1b) and their role in catalysis. With the exception of bulk TiO₂, the structure of these non-perfect species is still debated. In the present work, we discuss the capability of the various Ti sites to adsorb ammonia, a point that is relevant in some important reactions catalyzed by TS-1 such as cyclohexanone ammoximation. Furthermore, it has been followed also the HPPO (hydrogen-peroxide-to-propylene-oxide) reaction that is one of the most investigated processes as it is an economically and ecologically superior technology since potentially water is the only waste product. Here we report the EXAFS and XANES results at Ti K-edge of different samples of TS-1 after the contact with NH₃ feed. Moreover, we studied the Ti L_{2,3}-edge of the same compounds, more sensitive in elucidating the nature of the chemical bonds of the active metal site with the reactants, during the dehydration and the reaction with NH₃, H₂O₂ and C₃H₆. All the experimental data were supported by XANES simulation using the DFT-optimized clusters of the most stable Ti species in MFI (24 independent sites) [Signorile et al. *J. Phys. Chem. C* **2018**, acs.jpcc.7b10104]

Methods

The EXAFS experiment was carried on *in situ* at Ti K-edge of TS-1a and TS-1b hydrated, activated at 500°C and after the NH₃ interaction at XAFS beamline (Elettra, Trieste). In addition, the XANES experiment at the L_{2,3}-edges of Ti was done in the new *operando* setup at APE-HE beamline at Elettra. The XANES spectra were collected for investigating the relation between the type of Ti species and their reactivity with some reagents (NH₃, H₂O₂ and C₃H₆). The data were analyzed with a theoretical support: DFT optimization and XANES simulation.

Results and discussions

We investigated the Ti local environment by means of EXAFS experiments on TS-1a and TS-1b hydrated, dehydrated and after the NH₃ interaction. Hence the coordination of Ti atom in the TS-1a and TS-1b was obtained with their relatively differences. Moreover, it was proved that the Ti sites adsorb NH₃ molecules. While the XANES at L_{2,3} edge of Ti were adopted to follow the

unoccupied electronic DOS of Ti atoms during the exposure to different reactants i.e. NH_3 , H_2O_2 and C_3H_6 . The changes in the XANES spectra due to the interaction between the Ti atoms and the gas were analyzed by XANES simulation using the DFT-optimized structures. In this way, it has been possible to identify different Ti sites and their relative percentage present in the TS-1. Moreover the XANES spectra highlighted the different behavior of the Ti defects after the exposure to NH_3 , H_2O_2 and C_3H_6 .

Conclusions

In this work we present a detailed analysis of EXAFS and XANES experiment conducted on the perfect tetrahedral and defective TS-1 with different treatments. These measurements have permitted to identify the kind of Ti species presented in the TS-1b compared with TS-1a. Moreover, the adsorption geometry of NH_3 on Ti species was obtained. In addition, we also derived important information on the reactivity of Ti in TS-1 with H_2O_2 and C_3H_6 .