Towards the Understanding of the Active Site-Distribution in Sn-Beta

Patrick Wolf², Maxence Valla³, Aaron J. Rossini¹, Aleix Comas-Vives³, Francisco Núñez-Zarur³, Anne Lesage³, Lyndon Emsley³, Christophe Coperet³, Ive Hermans¹*

¹University of Wisconsin, Madison, Department of Chemistry. 1101 University Ave., 53706 Madison, WI (USA)
²ETH Zurich, Department of Chemical and Applied Biosciences. Vladimir Prelog Weg 2, 8093 Zurich (Switzerland)
³Centre de RMN à Très Hauts Champs, Institute de Sciences Analytiques, Université de Lyon (CNRS/ENS Lyon/UCB Lyon1), 69100 Villeurbanne (France)

*hermans@chem.wisc.edu

Introduction

Sn-Beta is a zeolitic material with isolated Sn(IV) Lewis acid centers embedded in a hydrophobic BEA zeolite framework. Due to its large pore architecture and strong Lewis acidity, this material has shown remarkable activity and selectivity in a number of industrially relevant processes, such as the Meerwein-Ponndorf-Verley (MPV) reaction [1] as well as the Baeyer-Villiger Oxidation utilizing hydrogen peroxide as the oxidant [2]. Moreover, Sn-Beta has gained a lot of attention in the upgrading of biomass-derived feedstocks, especially in the isomerization of monosaccharides [3] and in the synthesis of lactates from sugars [4] where promising results have been obtained. Industrial implementation, however, is still lacking, due to the restrictions associated with the catalyst synthesis. Therefore new post-synthetic methods for the preparation of these attractive materials have recently been proposed [5]. Commercially available Al-Beta zeolite is dealumminated by means of acid leaching, followed by the incorporation of tin into the newly created vacant T-sites. How these new materials compare in terms of their material characteristics, such as the nature of the active site or the positioning of the tin within the Beta framework with the traditional Sn-Beta zeolites is still an open question, which will be addressed in this work by combining advanced NMR techniques with DFT calculations and catalytic activity tests.

Methods

Dynamic Nuclear Polarization Surface Enhanced NMR Spectroscopy (DNP-SENS) was used to determine chemical shift anisotropy (CSA) parameters, defined as the isotropic chemical shift (δiso), the span (Ω) and the skew (κ), of each site present in the different materials. To correlate these observations directly to the local structure of the Sn environment, DFT calculations on cluster models of the different T-sites present in the Beta zeolite were carried out so that local structures can be suggested for the each site. Catalytic activity tests of the materials under investigation in test reactions, such as the aqueous phase glucose isomerization and the MPV reaction of cyclohexanone in 2-butanol were performed in batch reactors and the reactions were followed by HPLC and GC-FID respectively. Complementary, Powder X-ray diffractograms, N₂ and H₂O adsorption measurements were performed.

Results and Discussion

Sn-Beta zeolites with a Sn loading of 1wt% were prepared following both, traditional hydrothermal and alternative post-synthetic preparation protocols. All prepared materials were then tested in the aqueous phase isomerization of glucose as well as in the MPV reaction of cyclohexanone in 2-butanol. While no significant difference was observed for the MPV reaction between the different materials, the hydrothermal Sn-Beta materials showed greater than 4 times higher initial turnover frequency compared to the post-synthetic materials. Various catalyst characteristics, such as the crystallinity and the hydrophobicity of the zeolite framework or the local environment and the nature of the active site could contribute to this observation. Indeed, differences in the water adsorption behavior of both materials were observed, in that the post-synthetic material adsorbed about 5 times the amount of water as the hydrothermal zeolite. Moreover, DNP-SENS cross polarization magic angle spinning experiments revealed the presence of different active sites in each of the materials (Figure 1). The experimentally observed CSA parameters of the active sites will be compared with DFT predictions.

Significance

This work gives fundamental insights into the nature of the active sites in Sn-Beta zeolites. We conclusively show that Sn-Beta zeolites prepared according to different methods show distinct NMR signatures corresponding to different types of active sites. Understanding the precise nature of the active site is important since it does not only allow for prediction of structure-activity relationships, but also helps to identify the sensitive parameters during synthesis, an important aspect on the path of the industrial implementation of this promising material.

References


Figure 1. 9.4 T 105 K ⁴¹Sn DNP-SENS magic-angle spinning cross-polarization spin echo spectra of hydrothermal Sn-Beta (top) and post-synthetic Sn-Beta (bottom).