Report

Sn in zeolite structures, effects of synthesis method on chemical environment.

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Water-tolerant Lewis acid (WTLA) catalysis is a famous methodology for organic synthesis in aqueous environment. In contrast to the conventional Lewis acids, WTLAs are not deactivated in the presence of water. Most recent catalytic advances with WTLAs reveal unusual selective conversion of renewable feedstock like carbohydrates; where Sn is mostly the Lewis acid of choice.[1] The material showing the highest activities en selectivities is often a Snβ zeolite, a zeolitic structure with Sn built into the framework.[2] The active site for catalysis of the Snβ zeolite has often been discussed in the last decade, the general agreement at this moment is that a partially hydrolyzed framework Sn^{4+} atom (Sn-OH) is at the base of the high activity of this material.[3] Unfortunately, the synthesis of this molecular sieve is not straightforward, and is hampered by long synthesis times (up to 40 days) and use of corrosive HF to ensure good crystallinity, but which prevent use on an industrial scale. In order to circumvent these problems, alternative synthesis methods for the Snβ are being investigated.
Recently, we developed a synthesis method to synthesize Snβ materials within two days by grafting Sn onto a dealuminated commercial beta zeolite, and have been testing this material for its catalytic properties. The material shows extraordinary activities per Sn-atom, which transcend the activity of the original Snβ.[4] Characterization of the material has shown the Sn to be built into the framework, as is with the traditional synthesis. Different pretreatment procedures yield materials with different catalytic activities for different reactions. This raises questions about the role of the Sn-OH species as the only catalytic active site in the zeolitic structure.

Preliminary Results of the measurements:
XAS of the post-synthetic synthesized Snβ materials showed that the local environment differs only slightly from the hydrothermally synthesized zeolites. This indicates that the proposed post-synthesis method is a good alternative for the hydrothermal synthesis of Snβ materials, despite being quicker (2 days vs. >20 days for post-synthesis and hydrothermal synthesis respectively), safer (no use of HF) and more economical (cheaper chemicals). The small difference in Sn-environment is related to the degree of anchoring (in amount of bonds) of the Sn-atom in the zeolite. The post-synthesized materials shows lower amount of bonds to the zeolite framework, hereby creating a more accessible catalytic site and possibly a more hydrolyzed Sn-species (Sn-OH species, which is recognizes as the active species for Sn-Lewis acid catalysis), which is in agreement with catalytic activity of the material.

Outlook:
The results obtained from the XAS measurement provide us a clear view of the active site of the Sn-based materials, and confirm with experimental data from both catalysis and characterization. Currently we are finishing characterization and we plan to publish these results in the first half of 2014.

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