World Academy of Science, Engineering and Technology
International Journal of Energy and Power Engineering
Vol:11, No:09, 2017

The Effect of Metal-Organic Framework Pore Size to Hydrogen Generation of Ammonia Borane via Nanoconfinement

Authors : Jing-Yang Chung, Chi-Wei Liao, Jing Li, Bor Kae Chang, Cheng-Yu Wang

Abstract : Chemical hydride ammonia borane (AB, NH3BH3) draws attentions to hydrogen energy researches for its high theoretical gravimetrical capacity (19.6 wt%). Nevertheless, the elevated AB decomposition temperatures (Td) and unwanted byproducts are main hurdles in practical application. It was reported that the byproducts and Td can be reduced with nanoconfinement technique, in which AB molecules are confined in porous materials, such as porous carbon, zeolite, metal-organic frameworks (MOFs), etc. Although nanoconfinement empirically shows effectiveness on hydrogen generation temperature reduction in AB, the theoretical mechanism is debatable. Low Td was reported in AB@IRMOF-1 (Zn4O(BDC)3, BDC = benzenedicarboxylate), where Zn atoms form closed metal clusters secondary building unit (SBU) with no exposed active sites. Other than nanosized hydride, it was also observed that catalyst addition facilitates AB decomposition in the composite of Li-catalyzed carbon CMK-3, MOF JUC-32-Y with exposed Y3+, etc. It is believed that nanosized AB is critical for lowering Td, while active sites eliminate byproducts. Nonetheless, some researchers claimed that it is the catalytic sites that are the critical factor to reduce Td, instead of the hydride size. The group physically ground AB with ZIF-8 (zeolitic imidazolate frameworks, (Zn(2-methylimidazolate)2)), and found similar reduced Td phenomenon, even though AB molecules were not 'confined' or forming nanoparticles by physical hand grinding. It shows the catalytic reaction, not nanoconfinement, leads to AB dehydrogenation promotion. In this research, we explored the possible criteria of hydrogen production temperature from nanoconfined AB in MOFs with different pore sizes and active sites. MOFs with metal SBU such as Zn (IRMOF), Zr (UiO), and Al (MIL-53), accompanying with various organic ligands (BDC and BPDC; BPDC = biphenyldicarboxylate) were modified with AB. Excess MOFs were used for AB size constrained in micropores estimated by revisiting Horvath-Kawazoe model. AB dissolved in methanol was added to MOFs crystalline with MOF pore volume to AB ratio 4:1, and the slurry was dried under vacuum to collect AB@MOF powders. With TPD-MS (temperature programmed desorption with mass spectroscopy), we observed Td was reduced with smaller MOF pores. For example, it was reduced from 100°C to 64°C when MOF micropore ~1 nm, while ~90°C with pore size up to 5 nm. The behavior of Td as a function of AB crystalline radius obeys thermodynamics when the Gibbs free energy of AB decomposition is zero, and no obvious correlation with metal type was observed. In conclusion, we discovered Td of AB is proportional to the reciprocal of MOF pore size, possibly stronger than the effect of active sites.

Keywords : ammonia borane, chemical hydride, metal-organic framework, nanoconfinement
Conference Title : ICHET 2017 : International Conference on Hydrogen Energy and Technologies
Conference Location : Rome, Italy
Conference Dates : September 18-19, 2017