

***In situ* S/TEM Reactions of Ag/ZrO₂/SBA-16 Catalysts for Single-Step Conversion of Ethanol to Butadiene**

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1,3-Butadiene (C₄H₆ or BD) is used for manufacturing a variety of synthetic rubbers, elastomers, and polymer resins, with products that include tires, golf balls, and Legos. BD price swings and concerns about future supply shortages have created an incentive to find alternative sources; producing BD from renewable ethanol is one promising option [1]. A bifunctional Ag/ZrO₂/SBA-16 catalyst with tailored acid and metal sites that is both active and selective for the production of BD from ethanol has been developed [2]. It was recently discovered that when operating under hydrogen, a mixture of 1- and 2-butenes are produced instead of BD; n-butenes can be used as fuel precursors [2]. By understanding the catalyst stability and selectivity under reaction conditions, a selective two-step conversion of ethanol to jet- and diesel-range hydrocarbons is envisioned. The aim of this research is to determine the structure-function relationships of the Ag/ZrO₂/SBA-16 catalyst and the role of Ag dispersions within the catalyst on performance using *operando* scanning transmission electron microscopy (S/TEM) and X-ray absorption spectroscopy (XAS).

In situ closed gas-cell microscopy was used to study a complex reaction sequence applied to the 4Ag/ZrO₂/SBA-16 catalyst. A commercially available *in situ* gas-cell system (Protochips Atmosphere™) was modified to include a water-vapor delivery system and a residual gas analyzer (RGA) for the *operando* experiments [3]. The catalyst was prepared via incipient wetness impregnation [2] and STEM analysis showed a uniform distribution of Ag particles (2.1±0.4nm) across the SiO₂ support. For the *in situ* STEM experiments, the fresh 4Ag/ZrO₂/SBA-16 catalyst was crushed in ethanol to decrease the catalyst size scale to fit within the 5 μm gap within the gas-cell [4]. A droplet of the suspension was placed on the silicon nitride window of a Protochips™ E-chip heater chip. The gas-cell was purged three times with nitrogen from 300 to 0.1 Torr to remove residual O₂. The pressure was set to 760 Torr (1 atm) and the gas-cell was filled with 100% N₂. The catalyst was heated at 5°C/min. to 325°C under flowing 100% N₂ and held for 1 hr. Figure 1a shows the catalyst during heating and after reaching 325°C with corresponding mass spectrum (dotted black color spectrum) shown in Fig. 2 with N and N₂ peaks at 14 and 28 amu, respectively. The Ag particles coarsened during heating above 200°C to 6.12±2.7nm. The gas was switched to 10%H₂/N₂ at 325°C and the catalyst was exposed for another hour. A corresponding mass spectrum acquired at this condition is shown in green in Fig. 2, with H₂, N, and N₂ peaks visible at 2, 14, and 28 amu, respectively. After 1 hr the Ag particles became more spherical with a finer dispersion and more uniform size of 4.98±0.7nm, which is consistent with XAS measurements (4.3nm). The change in particle morphology could be related to the formation of metallic Ag as was detected by XAS in H₂/He at 325°C. At 325°C the gas was switched to 22% ethanol vapor and H₂ and held for 1 hr; corresponding gas composition shown by the red spectrum in Fig. 2; the ethanol peak at 46 amu was detected confirming its presence in the flowing media. There was no significant change in the Ag particles size from the previous step indicating their stability during exposure to the mixture of ethanol and H₂. After the final reaction step their average size was 4.86 ±1.0 nm. Diffractograms generated from the particles suggest the

existence of metallic silver, which further supports the stability of the catalyst. In summary, these studies show the first ever experiments using *operando* S/TEM capabilities to perform a complex reaction sequence that will enable future studies under “real” conditions to understand catalyst performance [5].

References:

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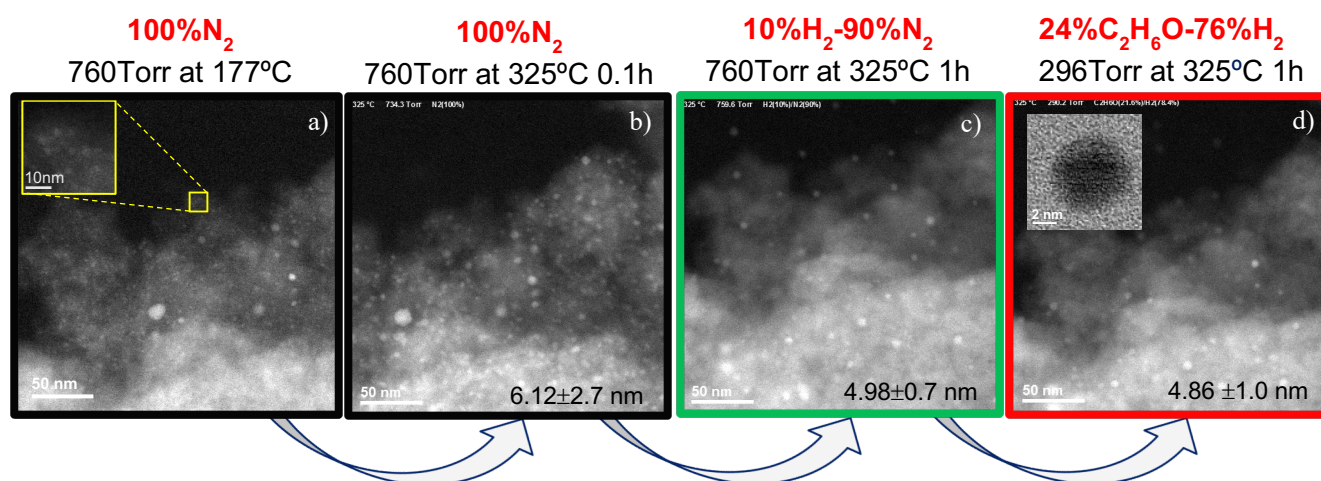


Figure 1. HAADF-STEM images of 4Ag/ZrO₂/SBA-16 catalyst acquired under series of reaction conditions: a) during heating at 177°C, b) at 325°C at 760 Torr under flowing N₂, c) at 325°C after 1 h at 760 Torr in 10% H₂-90% N₂, and d) at 325°C for 1 h at 760 Torr in the mixture of ethanol vapor and H₂.

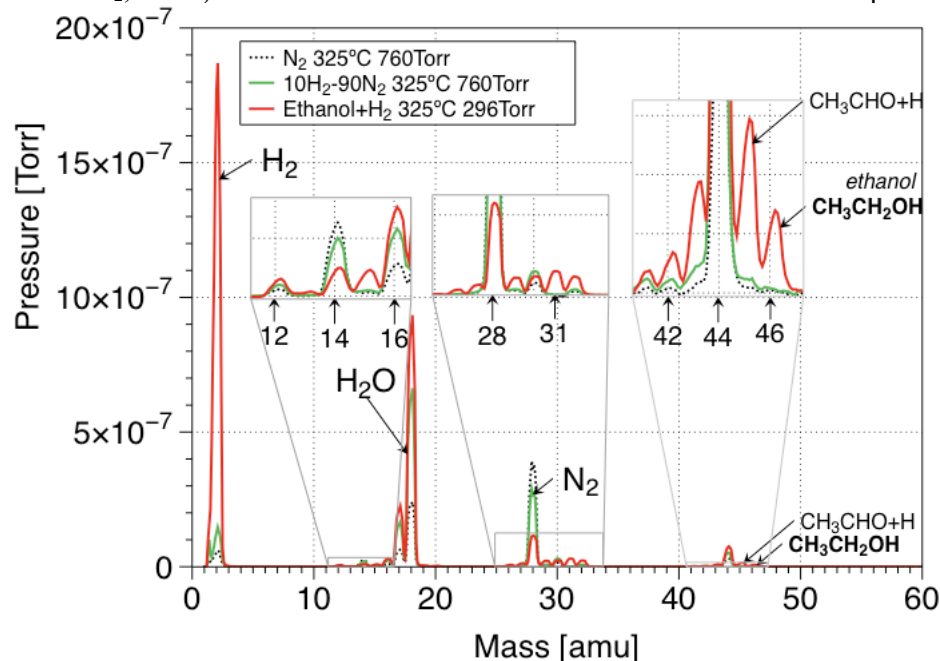


Figure 2. Color-coded mass spectra corresponding to each condition shown in Fig. 1. Mass spectra acquired during *in situ* STEM reaction at the exit side of the TEM holder.