

Ceria is a well-known oxygen storage catalyst widely used for the exhaust system of automobiles to remove pollutants via selective or complete oxidation processes [1-4]. It is also known for reforming processes of ethanol or methane for hydrogen production, solid oxide fuel cell application, and methanol synthesis and water gas shift reactions [2-4]. The success of ceria-based materials is mainly ascribed to the unique combination of high oxide-ion diffusivity with the redox cycle of Ce³⁺ and Ce⁴⁺ states [3]. The introduction of a metal into the ceria lattice is an efficient and versatile way of enhancing these unique properties. It has been shown that ceria catalysts modified with minute amount of lanthanum, zirconium, or hafnium exhibit a lower energy for the creation of oxygen vacancies, which boosts the redox behavior and thus the oxidation activity. [5].

Recently, ceria has been shown to catalyze the partial hydrogenation of propyne with a high selectivity [6-8]. Based on density functional theory (DFT) calculations and experimental results, it's proposed that the hydrogenation reaction goes through a six-membered ring transition state involving H₂, H atoms and propyne [6]. The adsorbed H atoms not only act as a hydrogen source for hydrogenation but also prevent the formation of oligomers by limiting the adsorption and diffusion of propene molecules. Although it required high temperature and slow space velocity, ceria offers a unique opportunity to design and develop a stable and easy regeneration catalyst system to effectively address the selectivity issue of selective hydrogenation reactions, including gas-phase hydrogenation of acetylene in ethylene for polyethylene industry [7,8] and selective hydrogenation of alkynes to alkenes in liquid phase.

In the 1st year period, we prepared supported Pd/CeO₂ catalyst with a low palladium loading of 500 ppm and 0.1-0.2% loadings of Pd in PdCeO_x prepared via the co-precipitation method. They were evaluated for selective hydrogenation of acetylene in large excess of ethylene. The results of Pd/CeO₂ catalysts are summarized below:

Performances of Pd/CeO₂: The performances of 500ppm Pd/CeO₂ catalysts under different reduction conditions for the selective hydrogenation of acetylene in ethylene are illustrated in Figure 1. For both unreduced and reduced samples, with H₂/C₂H₂/C₂H₄ ratio of 3/1/99 and 60,000 cc/g/h space velocity as shown in Figure 1(a), acetylene conversion plots exhibit the same tendency. With increasing temperature, the acetylene conversion first increased slowly, then turned to increase quickly and finally reached and remained at ~100%. For the unreduced samples, negligible amount of acetylene was consumed during the first 10 min of reaction at temperature below 56 °C. Acetylene conversion increased gradually above 56 °C and before 100 °C. Above 100 °C the conversion increased quickly, and finally reached around 100% at and above 158 °C. On the other hand, acetylene conversion curve of the sample reduced at 100 °C showed a lower increasing slope and the conversion achieved ~100% at a much higher temperature, 164 °C. While a higher increasing slope was exhibited for the sample reduced at 250 °C, its conversion of ~100% was achieved at a lower temperature of 128 °C. Acetylene conversions for samples reduced at 100 °C and 250 °C were higher than that of the unreduced one in the temperature ranges of 56-125 °C and 100-158 °C, respectively. It's noted that the activity of ceria was also tested for comparison and its acetylene conversion remain close to zero in the whole temperature range of 50-200 °C.

As shown in Figure 1(b), the ethylene selectivity of all three samples remained at around 100% and then underwent a huge drop when the temperature and acetylene conversion increase. For the unreduced sample, ethylene selectivity remained at ~100% before 128 °C and then dropped to 34% and remained almost constant until 200 °C. For samples reduced at 250 °C and 100 °C, the selectivities dropped to a negatively values of -26% at 110 °C and -63% at 86 °C, respectively. Although the selectivity increased as the temperature further increased, it was only -11% and -18% at 200 °C for the samples reduced at 250 °C and 100 °C, respectively.

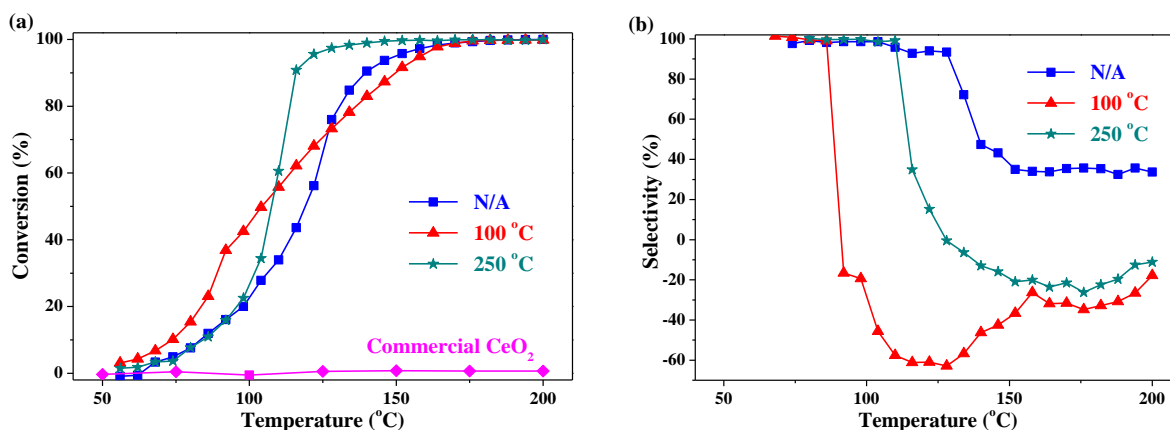


Figure 1. (a) Acetylene conversion and (b) ethylene selectivity over 500 ppm Pd/CeO₂, calcined at 450°C, without reduction, and reduced at 100 °C and 250 °C.

In comparison with the reduced Pd/CeO₂ catalyst, no significantly differences in acetylene conversion and a higher ethylene selectivity in high temperature range were observed for the unreduced sample. In this context, we proposed that Pd/CeO₂ catalysts could be activated in situ during reaction test since palladium could be reduced room temperature by CO and the pre-reduction process is not essential any more. Hence, unreduced sample was used to run the reaction test in the following experiments of calcination effect.

Calcination Temperature Effect: Calcination temperature effect on acetylene conversion and ethylene selectivity is illustrated in Figure 2. Pd/CeO₂ catalysts were used directly and no pre-reduction was conducted. Acetylene conversion decreases as the calcination temperature increases in the reaction temperature range of 50–200 °C, as shown in Figure 2(a). The conversion for samples calcined at 300 °C and 450 °C could reach 100% at above 146 °C and 158 °C, respectively. However, it was only 94% and 72% even at 200 °C for samples calcined at 600 °C and 800 °C, respectively. For samples calcined at 300 °C and 450 °C, as shown in Figure 2(b), ethylene selectivity went through a big drop at temperature of 104 °C and 128 °C, and that jumped to -2% and 34% at 200 °C, respectively. However, it still kept at 100% even at 200 °C for both samples calcined at 600 °C and 800 °C. This result of 100% ethylene selectivity is very interesting. Based on the literature, there is a possibility of forming PdCeO_x or Pd-O-Ce surface species [9,10]. However, due to the low loading of Pd in this study and there is no direct way to characterize the surfaces, we assume it's due to the contribution of extremely high palladium dispersion caused by strong interaction between palladium and ceria after high temperature calcination, although the palladium dispersion wasn't showed clearly due to the effect of hydrogen spillover.

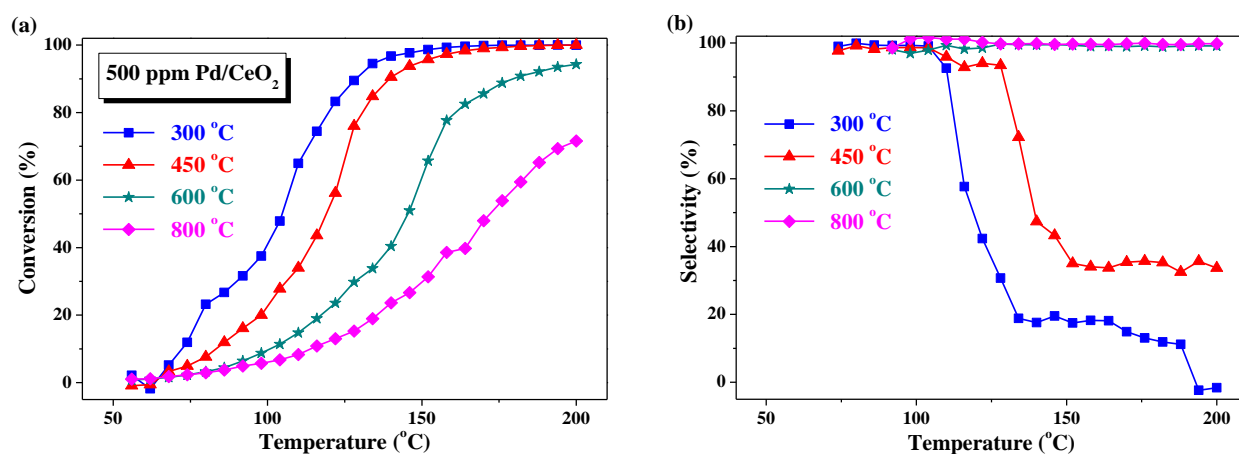


Figure 2. Effect of calcination temperature on (a) acetylene conversion and (b) ethylene selectivity over 500 ppm Pd/CeO₂ catalyst.

Impact of the Research: This project has provided significant amount of support for PI to mentor and train two undergraduate students during the academic semesters and two Master students during the summer. Two undergraduates successful finished their BS degrees in Spring 2018 and one of them continue her pursue of PhD degree in material science & engineering. Two master students are scheduled to finish their theses and MS degrees in Fall 2018.

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