

## Promotional Effect of Indium on the Kinetic Behaviors of Palladium Catalysts for Selective Hydrogenation of Acetylene

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### Highlights

- Activity, selectivity and anti-coking performance was enhanced by addition of In;
- Detailed characterization and DFT calculation was conducted;
- Electronic modification and geometric isolation of Pd sites has been confirmed.

### 1. Introduction

Palladium supported on metal oxide is commonly used as a catalyst for acetylene hydrogenation in ethylene industry, but exhibits limited selectivity and stability, due to the smaller barrier for ethylene hydrogenation than that for desorption and readily formed palladium hydride during hydrogenation [1]. To improve the catalytic performance, a second metal is usually introduced to modify the electronic and geometric structure of Pd catalysts. Recently, it was indicated that the specific activity of Pd in the unsupported intermetallic InPd<sub>2</sub> is much higher than that of elemental Pd, which makes Pd-In a very promising catalyst for industrial applications [2]. However, very little has been explored regarding the role of indium in the supported Pd-In catalyst, which may be different from that in the unsupported catalyst due to the particle size effect and the presence of support. To this end, we employed a co-impregnation method to prepare supported Pd-In nanoparticles on Al<sub>2</sub>O<sub>3</sub> (Pd-In/Al<sub>2</sub>O<sub>3</sub>), which exhibited preferable kinetic behaviors in acetylene hydrogenation. Combined catalyst characterizations and kinetic study revealed that indium promotes the Pd sites mainly by site isolation and electronic modification, which further modified the kinetic behaviors of Pd/Al<sub>2</sub>O<sub>3</sub>.

### 2. Methods

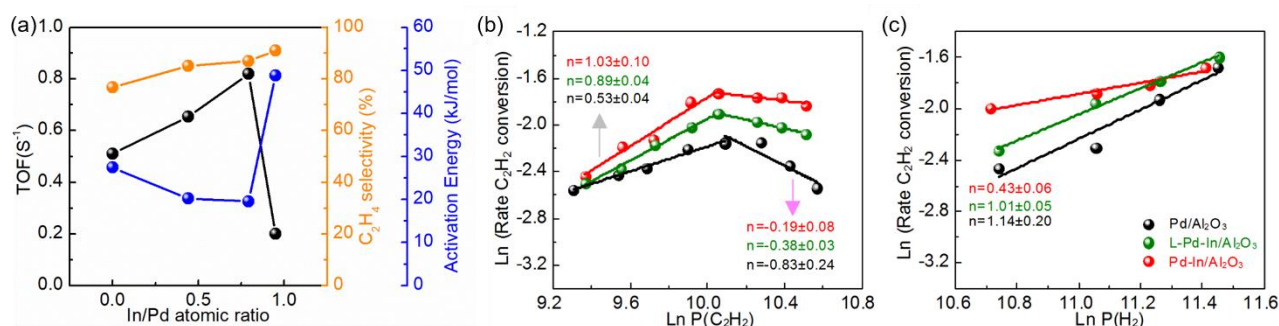
The catalysts were prepared by an impregnation method and investigated by detailed characterization and DFT calculation. The catalytic testing and kinetic studies were carried out on a  $\mu$ BenchCAT system (Altamira Instruments, USA) equipped with a stainless steel tube reactor.

### 3. Results and discussion

As revealed by XRD, HR-TEM and STEM-EDS line scan profiles, the as-prepared Pd-In/Al<sub>2</sub>O<sub>3</sub> was an alloyed catalyst. Pd-In/Al<sub>2</sub>O<sub>3</sub> exhibited higher activity and selectivity than Pd/Al<sub>2</sub>O<sub>3</sub> at temperatures from 30 to 70 °C. The catalysts with different In/Pd atomic ratios, one higher and one lower than that of Pd-In/Al<sub>2</sub>O<sub>3</sub> (denoted as H-Pd-In/Al<sub>2</sub>O<sub>3</sub> and L-Pd-In/Al<sub>2</sub>O<sub>3</sub>) both showed lower activities than Pd-In/Al<sub>2</sub>O<sub>3</sub>. The TOFs for acetylene hydrogenation based on metal surface area measured by H<sub>2</sub>-chemisorption were plotted as a function of the In/Pd atomic ratio. As seen in **Figure 1a**, the TOF, i.e., reaction rate, shows a strong dependence on the In/Pd atomic ratio, and the optimum appears at In/Pd atomic ratio of 0.8 (Pd-In/Al<sub>2</sub>O<sub>3</sub>). The dependence of activation energies on the In/Pd atomic ratio is opposite to that of reaction rate; the lowest activation energy was found on the catalyst with an In/Pd atomic ratio of 0.8. Ethylene selectivity increases concurrently with the In/Pd atomic ratio.

As shown in **Figure 1b**, the reaction rates over all catalysts increase monotonically with C<sub>2</sub>H<sub>2</sub> partial pressure at the low levels. The reaction orders with respect to C<sub>2</sub>H<sub>2</sub> obtained from the slopes of the linear curves increase with the content of In in the catalysts. However, the reaction rates decrease with the C<sub>2</sub>H<sub>2</sub>

partial pressure at the relatively high level, showing negative reaction orders. The negative  $C_2H_2$  pressure dependence indicates a strong adsorption of  $C_2H_2$  on the Pd surface, which lowers the availability of the vacant sites for  $H_2$  adsorption and dissociation and hence leads to a  $H_2$ -starved surface. The reaction order of  $C_2H_2$  for  $Pd/Al_2O_3$  is -0.83, which is in agreement with the value of -0.87 reported by Riyapan et al [3]. The reaction orders of  $C_2H_2$  for  $L-Pd-In/Al_2O_3$  (-0.38) and  $Pd-In/Al_2O_3$  (-0.19) are less negative than that for  $Pd/Al_2O_3$  (-0.83). As seen in **Figure 1c**, the reaction rates over all catalysts increase monotonically with the  $H_2$  partial pressure. Correspondingly, the reaction orders with respect to  $H_2$  decrease in the order  $Pd/Al_2O_3 > L-Pd-In/Al_2O_3 > Pd-In/Al_2O_3$ . The more positive  $H_2$  dependence of  $Pd/Al_2O_3$  also suggests the  $H_2$ -starved Pd surfaces, which is in good accordance with the competitive adsorption of both  $H_2$  and  $C_2H_2$  on the active sites in the Langmuir-Hinshelwood mechanism.



**Figure 1.** (a) Turnover frequency of acetylene conversion (black), ethylene selectivity at 30 °C (orange) and activation energy (blue) as a function of the In/Pd atomic ratio.; (b) The dependence of reaction rate on the partial pressure of  $C_2H_2$  at  $H_2$  pressure of 60.3 kPa; (c) The dependence of reaction rate on the partial pressure of  $H_2$  at  $C_2H_2$  pressure of 20.1 kPa.

To understand the promotional effect of indium on the kinetic behaviors, the structure of catalysts were investigated by detailed characterization, including CO-DRIFTS, XPS,  $C_2H_4$ -DRIFTS and  $C_2H_4$ -TPD. The results indicated that the isolation of Pd site and electron transfer from In to Pd weakened the adsorption strength of Pd active sites, which was further confirmed by the DFT calculations for the adsorption energies of  $C_2H_2$  and  $C_2H_4$ . Due to the weakened adsorption strength, the coverage of  $C_2H_2$  on the surface of  $Pd-In/Al_2O_3$  is smaller than that on  $Pd/Al_2O_3$ . That indicates that the activation of hydrogen on the much less crowded surface of  $Pd-In/Al_2O_3$  is easier, which accounts for the increased reaction rate on  $Pd-In/Al_2O_3$  (**Figure 1a**). Also, the adsorption of  $C_2H_4$  is weakened on the electron-rich and isolated Pd sites, which improves the selectivity to  $C_2H_4$ . As revealed by the structure characterization, the electron transfer in  $L-Pd-In/Al_2O_3$  is modified to a less extent than that in  $Pd-In/Al_2O_3$ . Thus, the adsorption of  $C_2H_2$  on  $L-Pd-In/Al_2O_3$  is stronger than that on  $Pd-In/Al_2O_3$ , which results in more crowded surface sites. The activation of hydrogen on the crowded surface is more difficult, leading to the decreased reaction rate (**Figure 1a**).

#### 4. Conclusions

The kinetic behavior of  $Pd/Al_2O_3$  for acetylene hydrogenation was promoted by alloying with indium. The isolation of Pd site and electron transfer from In to Pd weakened the adsorption strength of  $Pd-In/Al_2O_3$  and thus decreased the coverage of  $C_2H_2$  on the active sites.  $H_2$  activation was promoted on the less crowded surface, which enhanced the reaction rate on  $Pd-In/Al_2O_3$ .

#### References

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#### Keywords

Acetylene hydrogenation;  $Pd/Al_2O_3$ ; Indium; kinetics