Selective semihydrogenation of alkynes to alkenes over solid acid supported palladium catalysts

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Abstract: Several solid acids were prepared by treatment of TiO_2 by H_2SO_4 and then used to support ~3.0 nm Pd NPs by impregnation and plasma reduction method. The prepared Pd catalysts were utilized to catalyze the selective semihydrogenation of alkynes to internal and terminal alkenes. The results showed that 0.5 wt% Pd NPs supported on the solid acid that was treated under optimal concentration of H_2SO_4 displayed excellent catalytic activity in terms of high alkyne conversion and excellent alkene selectivity.

Keywords: Alkynes, semihydrogenation, Pd catalyst, solid acid**.**

1. Introduction

The selective semihydrogenation of alkynes to alkenes has drawn much attention because of the construction of numerous valuable compounds, including bioactive molecules, natural products, flavors, and industrial materials.[1,2] Tremendous catalysts, especially Pd, Ni or Au nanocatalysts, have been under investigation for the conversion of alkynes into alkenes. [3,4] Among them, Lindlar catalyst was widely used.[5] While further large application is hampered by the disadvantages of Lindlar catalyst, such as the requirement of a toxic lead salt, partial isomerization of Z-alkene to E-alkene, double-bond shifting as well as the lack of highly reproducible results. Besides, only internal alkynes are selectively hydrogenated into desired alkenes, and over-hydrogenation often happens rapidly into alkanes from alkenes. From the point view of the sustainable development and the protection of environment, novel catalysts should be developed with remarkable features of nontoxicity, robustness and high recyclability. Herein, ~3.0 nm Pd NPs were deposited on the solid acid by the combination of impregnation method with plasma reduction technique, and then used to efficiently catalyze the selective semihydrogenation of alkynes to alkenes.

2. Experimental

2.1 Synthesis of solid acid (SO_4^{2-}-TiO_2)

In a typical synthesis, TiO_2 (Degussa P25) was submerged in one n M H_2SO_4 solution (n = 0.5, 1, 2 and 3), and the mixture was sonicated for 5 min. This effectively drove the H_2SO_4 solution into the pore networks, leading to a homogeneous adsorption of SO_4^{2-} on the surface of TiO_2.[6] After that, the mixture was stirred at 50 °C to remove water. The resulting solids were calcined at 450 °C for 3 h to obtain the SO_4^{2-}/TiO_2 solid-acid, and the SO_4^{2-}/TiO_2 solid acid were denoted as ST-n (n = 0.5, 1, 2 and 3 M H_2SO_4).

2.2 Synthesis of Pd/ST-n catalyst

Solid acid ST-n was mixed with the required amount of $Pd(NO_3)_2$ in water in one beaker (the weight percent of Pd to ST-n was 0.5%), and then dried overnight under vacuum at room temperature. The as-prepared Pd/ST-n was transferred to the plasma generator and reduced with H_2. The resulting catalysts were named as 0.5% Pd/ST-n (n=0.5, 1, 2 and 3).

3. Results and discussion

The high-angle annular dark-field scanning transmission electron microscopy (HAADF–STEM) images of 0.5% Pd/ST-2 catalyst were shown in **Figure 1**. It is found that the crystal morphology of ST-2 support is very different from that of the pristine TiO_2. In addition, Pd NPs with the size of ~3.0 nm were synthesized and highly dispersed on ST-2 support.

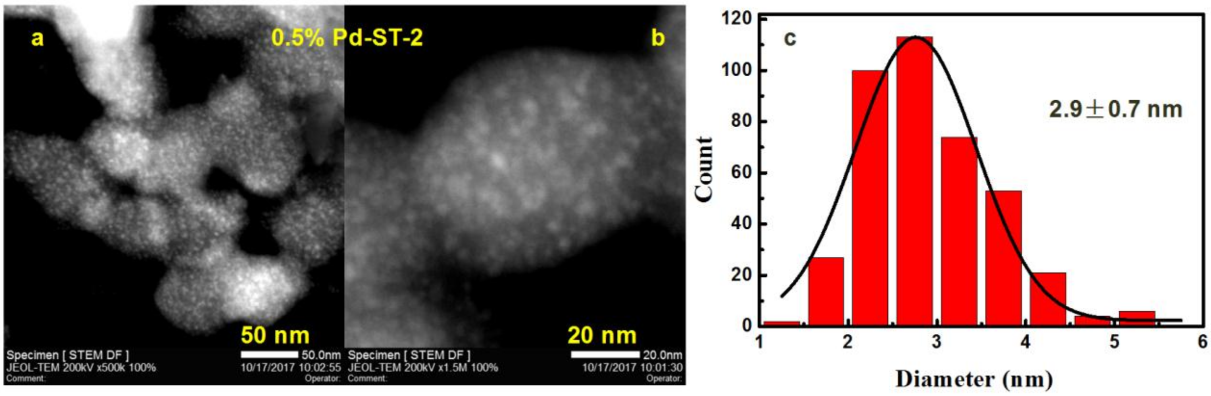

Figure 1. HAADF-STEM images of 0.5% Pd/ST-2 (a), (b) and the corresponding size distribution of Pd NPs.

The semihydrogenation of phenylacetylene (**Figure 2a**) and diphenylacetylene (**Figure 2b**) was catalyzed by 0.5 % Pd/TiO_2 as well as 0.5% Pd/ST-n, (n= 0.5, 1, 2 and 3). As shown in **Figure 2a**, high selectivity of stryrene is observed over all the catalysts, while only 0.5% Pd/ST-1 and 0.5% Pd/ST-2 can display high conversion of phenylacetylene. As shown in **Figure 2b**, all the catalysts show excellent diphenylacetylene conversion (> 99%). However, only 0.5% Pd/ST-n (1, 2 and 3) displays high selectivity of diphenylethene, and over-hydrogenation of diphenylacetylene to diphenylethane happens on 0.5% Pd/TiO_2 and 0.5% Pd/ST-0.5.

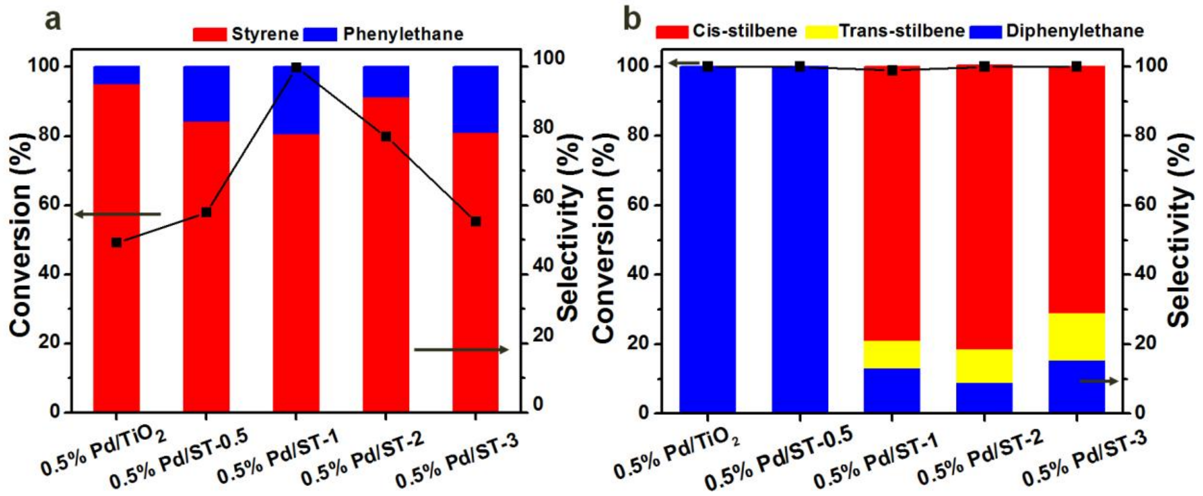

Figure 2. Semihydrogenation of alkynes catalyzed by 0.5% Pd/TiO_2 and 0.5% Pd/ST-n (n=0.5, 1, 2, 3): (a) phenylacetylene to styrene and (b) diphenylacetylene to diphenylethene.

4. Conclusions

In summary, a series of solid acid (ST-n) were prepared by treatment of TiO_2 by H_2SO_4 with different concentration, and then used to support ~3.0 nm Pd NPs by the method combination of impregnation and plasma reduction. It was found that in the selective hydrogenation of phenylacetylene and diphenylacetylene over Pd/ST-n catalysts, H_2SO_4 concentration played an important role in determining alkyne conversion and alkene selectivity, respectively.

References

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