

Product Selectivity Controlled by Zeolite Crystals in Reactions over Palladium Catalysts

Liang Wang,^{a,*} Feng-Shou Xiao^{a,*}

^a Key Lab of Applied Chemistry of Zhejiang Province, Department of Chemistry, Zhejiang University, Hangzhou 310028, China.

*Corresponding author: liangwang@zju.edu.cn; fsxiao@zju.edu.cn

Abstract: This work delineates first example for controlling product selectivity in metal-catalyzed hydrogenation of biomass by zeolite crystals. The key to this success is to combine the advantages of both Pd nanoparticles (highly active sites) and zeolite micropores (controllable diffusion of reactants and products), which was achieved from encapsulation of the Pd nanoparticles inside of Silicalite-I zeolite crystals as a core-shell structure (Pd@S-1). In the hydrogenation of biomass-derived furfural, the furan selectivity over the Pd@S-1 is as high as 98.7%, outperforming the furan selectivity (5.6%) over conventional Pd nanoparticles impregnated with S-1 zeolite crystals (Pd/S-1). The extraordinary furan selectivity in the hydrogenation over the Pd@S-1 is reasonably attributed to the distinguishable mass transfer of the hydrogenated products in the zeolite micropores.

Keywords: Pd catalyst; hydrogenation; biomass; nitroarene; diffusion

1. Introduction (11-point boldface)

Selective transformation of renewable biomass-derived feedstocks plays a key role in sustainable production of biofuels and fine chemicals. Up to now, many economically viable processes have been developed for the conversion of biomass. For example, pyrolysis or hydration of lignin and cellulose, which contain more than 30% of the organic carbon on earth, to produce various platform chemicals of phenols, levulinic acids, and furfurals has been deemed to be promising alternatives to crude oil. In these processes, it is notable that the biomass derived chemicals normally have relatively high oxygen content, which strongly limits their applications. Therefore, upgrading the biomass-derived chemicals by hydrogenation to selectively remove the oxygen groups in the chemicals is strongly desirable. However, it still has a challenge to control the product selectivity in biomass hydrogenation yet because these reaction pathways with many undesirable reactions are very complex.

2. Results and discussion

Here we report a generalized strategy for preparation of excellently selective and highly active catalysts by encapsulation of metal nanoparticles inside of microporous silicalite-I (S-1) zeolite as core-shell structures (metal@zeolite), where the metal nanoparticles serve as catalytically active sites and the zeolite micropores control the product selectivity by changing molecular diffusion. Considering that Pd nanoparticles are highly active but poor selective in the biomass hydrogenation and S-1 zeolite is easily synthesized, a Pd@S-1 was successfully prepared from solvent-free crystallization of a solid mixture including Pd nanoparticles, amorphous silica, and organic structural directing agent (OSDA).²⁴ As expected, the Pd@S-1 is highly active and excellently selective in the hydrogenation of biomass derived furfural, giving furan selectivity as high as 98.7% with furfural conversion of 91.3%. In contrast, conventional supported catalysts show relatively low furan selectivities, which are due to the complexity of reactive pathways and difficulty in controlling the selectivity.

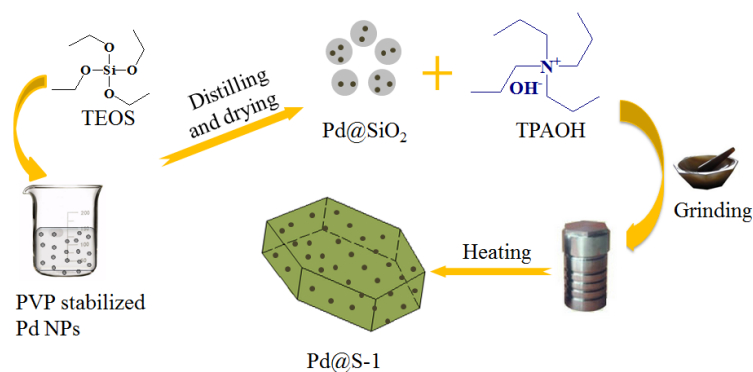


Figure 1. Scheme for the synthesis of zeolite fixed metal nanoparticle catalysts.

4. Conclusions

In summary, we show a novel strategy to control the furan selectivity in the furfural hydrogenation over a core-shell structural Pd@S-1 catalyst synthesized from a solvent-free crystallization. This catalyst efficiently combines high activity of the Pd nanoparticles and excellent selectivity of zeolite micropores, giving the furan selectivity as high as 98.7% with furfural conversion at 91.3%. In addition, this catalyst is easily regenerated by calcination at 550 °C. The strategy for preparation of the Pd@S-1 with high activity, excellent selectivity, and superior regenerated activity in the furfural hydrogenation should be potentially important for designing and developing highly efficient heterogeneous catalysts in the future.

References

1. J. Zhang, L. Wang, Y. Shao, Y. Wang, B. C. Gates, F.-S. Xiao, *Angew. Chem. Int. Ed.* 2017, DOI: 10.1002/anie.201703938
2. L. Wang, G. Wang, J. Zhang, C. Bian, X. Meng, F.-S. Xiao, *Nat. Comm.* 8 (2017) 15240.
3. C. Wang, L. Wang, J. Zhang, H. Wang, J. P. Lewis, F.-S. Xiao, *J. Am. Chem. Soc.* 138 (2016) 7880-7883.