Pd/Lewis Acid Synergy in Macroporous Pd@Na-ZSM-5 for Enhancing Selective Conversion of Biomass

Jia-Wen Liu, Si-Ming Wu, Li-Ying Wang, Ge Tian, Yuan Qin, Jing-Xian Wu, Xiao-Fang Zhao, Yan-Xiang Zhang, Gang-Gang Chang, Lu Wu, Yue-Xing Zhang, Zhao-Fei Li, Cheng-Yu Guo, Christoph Janiak, Silvia Lenaerts and Xiao-Yu Yang

Pd nanometal particles encapsulated in macroporous Na-ZSM-5 with only Lewis acid sites have been successfully synthesized by a steam-thermal approach. The synergistic effect of Pd and Lewis acid sites has been investigated for significant enhancement of the catalytic selectivity towards furfural alcohol in furfural hydrosyngeneation.

Nanostructured palladium (Pd) metal, as one of the most efficient catalysts for hydrogenation reactions, has been widely used for biomass conversion. However, many issues need to be addressed for the practical application of Pd nanoparticles, such as fast kinetics, high stability, and especially selectivity enhancement. Confinement of Pd nanometal in a zeolite matrix is a promising way to a catalyst design that shows significant synergy by combination of well-defined acid sites, shape selectivity, and outstanding stability. Zeolite-confined Pd show unique cascade effects on a molecular scale, and thus enables spatially confined catalysis similar to enzyme catalysis. The acid sites play a key role in sustainable production of biofuels, such as adsorption promotion of reactants and electronically influence of Pd. In the meantime, the confined Pd particles in the acidic zeolite will also strongly influence the state of the acid sites, contributing to the synergy effects of Pd and acid sites. Bronsted acid sites, arising from the framework Al species in highly crystalline zeolites, have been studied for selective conversion. However, the strong Bronsted acid sites often lead to the formation of coke and the low stability of AI sites in the zeolite framework, which would decrease the catalyst lifetime. Lewis acidity might circumvent these two problems due to its weaker acidity property and higher stability. It is therefore of great interests to understand the role of Lewis acid sites in Pd/zeolite catalysts, and thus achieve the high activity, selectivity and stability of Pd/zeolites during selective transformation of renewable biomass-derived feedstocks.

However, most studies focus on the Bronsted acid sites in zeolite catalytic systems, and there are rare reports on the design and study of Pd/Lewis acid sites. Generally, Bronsted acid sites are attributed to the framework Al in highly crystallized zeolites, which is commonly obtained by hydrothermal process. Therefore, to design Pd/Lewis sites system, we present a direct steam-thermal crystallization approach to obtain low crystallized Pd/macroporous ZSM-5 (denoted as Pd@ZSM-5) with a large amount of extra framework Al. For decreasing the number of Bronsted acid sites, H₂O⁺ ions in ZSM-5 are exchanged by Na⁺ ions. Macroporosity is introduced in ZSM-5, for increasing the contact of the extra framework Al. The catalysts are then applied in the hydrosyngeneation of furfural (FFL), which is an important and highly unsaturated intermediate in the production of biofuels.

Figure 1a illustrates the procedure for the synthesis of Pd@ZSM-5. First K₂PdCl₄ was impregnated in mesoporous silica
The unique catalytic properties of zeolite-encapsulated Pd nanoparticles are investigated with the model reaction of hydroconversion of FFL, where various products will form based on the diverse catalytic steps derived by different active sites (Figure 3a). The reaction is carried out in the presence of a mixture of Pd@ZSM-5, Pd@ZSM-5-W, and Pd@ZSM-5-S. The selectivity of the products is determined by gas chromatography (GC) analysis. The results show that Pd@ZSM-5 has the highest selectivity for furfural alcohol (FAL) compared to the other catalysts, with yields of 57%, 52%, and 48%, respectively. The selectivity of furfural alcohol is confirmed by 2D correlation spectroscopy (COS) NMR experiments, which indicate the presence of aldehydes and ketones as intermediates in the conversion process. The unique catalytic properties of zeolite-encapsulated Pd nanoparticles are attributed to the synergistic effect of the metal nanoparticles and the acidic sites of the zeolite framework. The results provide new insights into the design of catalysts for the selective conversion of biomass-derived materials.
productions of the catalysts (Pd/Na-ZSM-5, Pd/H-ZSM-5, Pd/S-1, and commercial Pd(C) using impregnation-reduction are considerably high (up to 86%), while the catalysts (Pd@Na-ZSM-5, Pd@H-ZSM-5 and Pd@S-1) using direct transformation show very low amounts of by-products (up to 40% over Pd@S-1). This suggests that the catalysts designed by our synthesis method greatly decreases the by-production and enhances the yield of value-added productions 2-methylfuran (2-MF) and 1,5-pentanediol (PDO) compared with samples obtained by common impregnation method. Very interestingly, only Pd@Na-ZSM-5 show significant selectivity of FAL, which is possibly due to the synergistic effect of Pd and acid sites in Pd@Na-ZSM-5.

The acidic microenvironment of this zeolite might significantly modulate the reaction pathways and product distribution in FFL hydroconversion.\textsuperscript{[7]} Firstly, the acid-base sites provided by the zeolite environment are investigated by NH\textsubscript{3} temperature-programmed desorption (TPD).\textsuperscript{[33]} The ammonia desorption peak in the temperature range of 50–200 °C (1.0 mmol NH\textsubscript{3}/g) in the NH\textsubscript{3}-TPD profile of Pd@Na-ZSM-5 (Figure S7) is observed, which is generally assigned to the weak acid sites. As comparison, Pd@H-ZSM-5 show larger amount of weak acid sites (1.8 mmol NH\textsubscript{3}/g). In the meantime, an additional peak ranging of 300–500 °C of Pd@H-ZSM-5 indicates the existence of strong acid sites (0.7 mmol NH\textsubscript{3}/g). Solid-state NMR is also a very powerful tool for probing the acid sites.\textsuperscript{[34,35]} To further study the Brønsted and Lewis acid sites and to gain insight into the spatial proximity/interaction between the acid sites in ZSM-5, \textsuperscript{1}H magic-angle-spinning (MAS)-NMR and 2D \textsuperscript{1}H double-quantum (DQ) MAS-NMR, both highly sophisticated pulse techniques, have been performed. And to avoid the influence of absorbed water, a pre-dehydration is required before measurement. Figure 4a, b shows the \textsuperscript{1}H MAS NMR spectra of Pd@Na-ZSM-5, Pd@Na-ZSM-5 and Na-ZSM-5 (Figure 4a), and Pd@H-ZSM-5, Pd/H-ZSM-5 and H-ZSM-5 (Figure 4b). Typically, protons residing at Brønsted acid sites, for example, bridging hydroxyls in zeolites, possess \textsuperscript{1}H in range of 3.6–5.6 ppm, whereas weakly acidic terminal hydroxyls, possibly caused by Lewis sites, tend to appear at 1.5–2.0 ppm.\textsuperscript{[33]} It is obvious that all Na\textsuperscript{+} ion exchanged ZSM-5 (Pd@Na-ZSM-5, Pd/Na-ZSM-5 and Na-ZSM-5) present the sharp and symmetrical signal peak near 2.4 ppm (Figure 4a), indicating the successful control of only Lewis acid sites. Meanwhile, all H-ZSM-5 based catalysts (Pd@H-ZSM-5, Pd/H-ZSM-5 and H-ZSM-5) show relatively strong signal of Brønsted acid sites at 5.1 ppm and weak signal of Lewis acid sites (Figure 4b).

To further obtain the information about interaction between acid sites of zeolite and Pd, the highly sophisticated pulse technique, 2D \textsuperscript{1}H DQ-SQ MAS NMR, is performed. As shown in Figure 4c, the signal at (2.4, 2.4) of Pd@Na-ZSM-5
indicates the spatial proximity of hydroxyl groups associated with external framework Al in the supercage, while the strong signal at (5.4, 5.4+5.4) of Pd@H-ZSM-5 (Figure 4d) indicates the main existence of neighboring Brønsted acid sites. Compared with Pd@Na-ZSM-5 and Na-ZSM-5, the H DQ-SQ MAS NMR spectrum of Pd@Na-ZSM-5 shows only the signal of Lewis acids, suggesting that the direct transformation could create the interaction between the Pd and Lewis acid sites, and the corresponding synergy of Pd and Lewis acid sites leads to significant enhancement of catalytic selectivity.

For further understanding the interaction between the Pd and Brønsted/Lewis acid sites, the X-ray photoelectron spectroscopy (XPS) (Figure 5a) and EPR (Figure 5b) are tested. The two peaks at around 334.5 eV and 339.9 eV of Pd@Na-ZSM-5 are corresponding to the Pd 3d_{3/2} and Pd 3d_{5/2} of Pd (0), respectively (Figure 5b). Chemical shift of Pd 3d spectra reflects the different states of Pd in each sample. Compared with Pd@S-1, the Pd 3d_{3/2} binding energy values of Pd@Na-ZSM-5 and Pd@H-ZSM-5 zeolites shift toward higher values by 0.3 eV and 0.4 eV, respectively (Figure 5a), which is due to the higher electron transfer from palladium to the zeolite framework in the acid environment. Similarly, the stronger signal of the EPR spectra in Pd@Na-ZSM-5 and Pd@H-ZSM-5 (Figure 5b) is also attributed to more active free-electrons than Pd@S-1.\(^{12}\) Considering the very high hydrogen activation of Pd, the saturation hydrogenation occurs over the Pd@H-ZSM-5, which is in good agreement with the catalytic result (the 2-MF % is higher than the Pd@Na-ZSM-5). The possible mechanism of selective hydrogenation by Pd/Lewis acid and Pd/Brønsted acid models are proposed in Figure 5c. In a Pd/Lewis acid system (Figure 5c, I), the synergistic effect of Pd and Lewis acid sites will promote the adsorption of H\(_2\) and the hydrogenation reaction, resulting in the formation of FAL. For Pd/Brønsted acid system (Figure 5c, II), the protons from bridging hydroxyls in H-ZSM-5 (Si–OH–Al) are more likely to attack the oxygen atoms in furan rings, resulting in the ring opening reaction. Pd that provides excellent hydrogen activation through homolytic H\(_2\) cleavage, leads to a saturation hydrogenation and even total hydrogenation to products like PDO. Therefore, different product distributions are obtained in Pd/Lewis acid and Pd/Brønsted acid system.

In summary, we have successfully designed Pd-encapsulated macroporous ZSM-5 zeolite with high stability. Pd@Na-ZSM-5 shows high selectivity of FAL in the biomass conversion. The interactions between Pd and the acid sites in zeolite has been investigated with multiple techniques and the mechanism of synergistic effect of Lewis acid and Pd is proposed. It is believed that this work provides a new insight for the investigation of highly selective zeolite-encapsulated metal catalysts.

Acknowledgements

We acknowledge a joint DFG-NSFC project (DFG JA466/39-1, NSFC grant 51861135313). This work was also supported by National Key R&D Program of China (2017YFC1103800), NSFC (U1662134, 21711530705), Jilin Province Science and Technology Development Plan (20180101208JC), HPNSF (2016CFA033), FRFCU (19lgzd16) and ISTCP (2015DFE52870).

Conflict of Interest

The authors declare no conflict of interest.

Keywords: Pd cluster · Lewis acids · confinement effect · synergistic effect · biomass conversion

![Figure 5](image_url)

**Figure 5.** (a) Chemical shift of Pd 3d\textsubscript{3/2} XPS spectra of Pd@S-1, Pd@Na-ZSM-5 and Pd@H-ZSM-5, (b) EPR spectra of Pd@S-1, Pd@Na-ZSM-5, Pd@H-ZSM-5 and Pd/C. (c) Schematic illustration of the selective hydrogenation of FFL over the model of (I) Pd/Lewis acid and (II) Pd/Brønsted acid.