

Pd Nanoparticles supported on a Microporous Covalent Triazine Polymer for Hydrogen production from Formic Acid Decomposition

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Abstract: Pd nanoparticles (NPs) supported on a microporous covalent triazine-based polymer (Pd/MCTP-1) was prepared and applied for formic acid decomposition at 323 K. The catalytic activity of Pd/MCTP-1 for the H₂ production was superior to those of Pd/MOFs (metal-organic frameworks), which was attributed to the two factors of i) monodisperse and smaller Pd NPs and ii) neutral pH of the reaction medium attained. Pd/MCTP-1 was highly stable and the catalytic activity was maintained up to three recycle runs.

Keywords: Formic acid decomposition, Pd nanoparticle, Covalent triazine-based polymer.

1. Introduction

Hydrogen is a clean energy source and essential with high usages in petrochemical industries. Among the liquid hydrogen storage materials, formic acid has been actively investigated owing to its abundance, low cost, and nontoxicity.¹ Easy hydrogen release by decomposition and reversible storage via hydrogenation of the captured CO₂ under ambient conditions also closely meet the criteria for the hydrogen carrier in the fuel cell applications.

Recently, a group of highly crosslinked polymeric porous materials with regular micropores have emerged as a promising candidate in a variety of applications such as gas storage,² drug delivery,³ and catalysis.⁴ They often have high surface areas, highly stability, hydrophobicity, and can easily be subjected to organic-functionalization,⁴ which offer new opportunities as a catalyst or support for liquid phase catalytic reactions. In this study, Pd nanoparticles (NPs) supported on a microporous covalent triazine-based polymer (Pd/MCTP-1) was prepared and tested as catalyst for formic acid decomposition. The catalytic activity of Pd/MCTP-1 was compared with other Pd NPs supported on different porous materials including MOFs (metal organic frameworks), and its superior activity was rationalized in terms of its physicochemical properties.

2. Experimental

MCTP-1 was prepared following the procedure reported by Puthiaraj et al.⁵ using a mixture of cyanuric chloride and 1,3,5-triphenylbenzene in dichloromethane (DCM) over anhydrous aluminum chloride catalyst. MCTP-1 was dispersed in water followed by adding Na₂PdCl₄ solution and stirred at 80 °C for 1 h. NaOH solution was then added to adjust the solution pH till pH =12, and the solution was kept under stirring. Subsequently, NaBH₄ was added under continuous stirring. The Pd/MCTP-1 catalyst was collected by filtration, washed with DI water, and dried at 80 °C for 12 h. For formic acid decomposition, a round flask reactor containing a given amount of catalyst in water was connected to a gas burette, pressure-equalizing funnel containing formic acid, and Ar gas line. A reaction was initiated by injecting the formic acid under vigorous stirring. The volume of the evolved gas was monitored by recording the displacement of water in the gas burette.

3. Results and discussion

Figure 1 shows the plots of the evolved gas ($\text{CO}_2 + \text{H}_2$) versus reaction time during the formic acid decomposition over the Pd-supported catalysts. Pd/MCTP-1 showed the best catalytic performance among the catalysts tested, and the turnover frequency (TOF) and the total gas production amount were ca. 1.6 and 1.8 times higher than those of the next best catalyst, Pd/MIL-101-DETA, respectively. These results with the characterization data in Figure 1 clearly established that Pd NPs size plays an important role such that the smaller the Pd NPs more active was the catalyst for the reaction. In the case of catalysts with Pd NPs larger than 6 nm (Pd/C, Pd/SBA-15, Pd/UiO-66, and Pd/MIL-101), the initial gas evolution rates and the total evolved gas amounts were very low. On the other hand, catalysts bearing Pd NPs ranging from 3.5~5 nm showed moderate catalytic activities; TOFs of Pd/UiO-66-NH₂ and Pd/MIL-101-DETA were approximately 5.3 and 10 times higher than those of counterparts without amine groups. Moreover, the amounts of total evolved gases also increased significantly by the introduction of amine groups on the MOF structures. The catalytic activity was also significantly affected by the pH of a reaction medium; undesirable recombination of the formate ion with a proton takes place in an acidic solution whereas competitive adsorption between the formate and hydroxyl ions takes place in a basic solution. Therefore, a neutral reaction medium is necessary to provide a more desirable chemical environment for catalysis. In the case of Pd/MCTP-1, the triazine groups may act as an excess proton scavenger and thus expedite the formic acid decomposition.

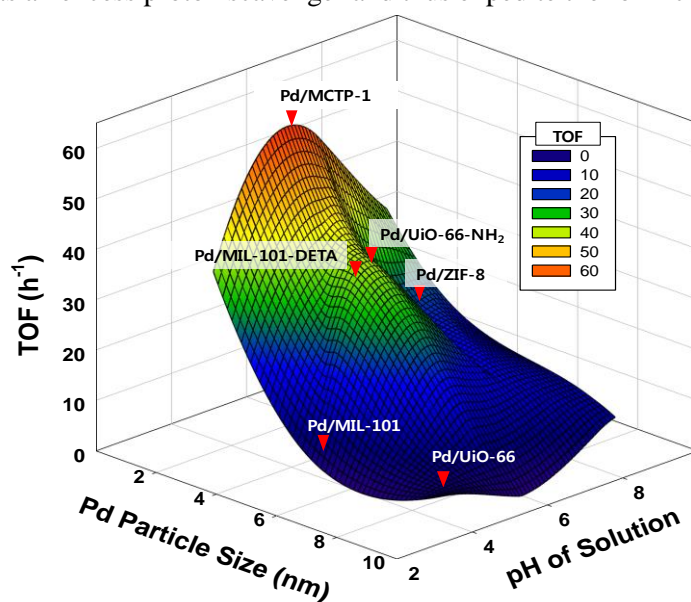


Figure 1. Effect of Pd particle size and pH of a reaction medium on the turnover frequency in HCOOH decomposition.

4. Conclusions

This study reports the successful application of Pd/MCTP-1 catalyst for formic acid decomposition under mild reaction conditions. The excellent catalytic activity clearly demonstrates the potential of triazine-based porous organic polymer as a supporting material for hydrogen production via formic acid decomposition.

References

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