

Bio Oil Steam Reforming over Mesoporous Hexagonal and Noncapsular Ni Nanoparticle Catalyst Prepared Using Post Loading and Co-Assembly Strategy

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Significance and Relevance

A series of Nickel (Ni) nanoparticle catalysts encapsulated on $Al_2O_3/SBA-15$ and $Al_2O_3/CNFs$ were prepared using a post loading strategy and co-assembly strategy, respectively. The novel approach addressed the potential Ni sintering issue during bio-oil steam reforming activity. Also, the CeO₂ was introduced to prevent coke formation. Both of post loading and co-assembly strategy could reached H₂ yield up to 75%. Further, the addition of CeO₂ improved H₂ yield up to 85%. Confirming that the mesoporous hexagonal and noncapsular catalyst design types could reach high H₂ and stability.

Preferred and 2nd choice for the topic: H₂ storage and transportation, green H₂ production, hydrogen vectors (1st), Fundamental advances in understanding catalysis (2nd) Preferred presentation: (Oral only / Oral preferred or Short Oral / Poster)

Introduction and Motivations

Steam reforming of bio-oil is possible to produce H₂ in large quantity, which has drawn wide attention in green energy. Acetic acid is frequently utilized as a model compound in steam reforming of bio-oil due to non-flammable, easy to store and much safe hydrogen carrier. Steam reforming of acetic acid has been extensively studied using a nickel (Ni) nonnoble-based catalyst with high activity due to its lower cost and higher availability compared to another noble-based catalyst. However, metal sintering and carbon deposition (coke) formation during the steam reforming reaction triggered catalytic deactivation in Ni-based catalysts. Based on previous studies, Ni nanoparticle catalyst needs support to stabilize Ni and enhance the catalytic activity. For instance, Ni catalyst prepared with Al₂O₃, most frequently used support, could reach high H₂ but still struggle with the catalyst deactivation.¹

Recently, several prepared catalyst have been utilized to prevent coke formation and agglomeration of Ni, including combining Ni/Al₂O₃ into SBA-15, as a silica support due to its mesopores properties.^{2,3} Further, the introduction of ceria (CeO₂), a promoter, could also help inhibit coke formation due to its rich oxygen storage capacity.¹ In fact, the strategy to prepare catalyst is crucial to obtain the final catalyst design with high diffusion through higher pore distribution inside catalyst, such as post loading strategy and co assembly strategy, these can be used due to precisely controlled Ni nanoparticle size, convenient, simple, and high stability,² which still lack applied in steam reforming of acetic acid. Besides, cellulose nanofibers (CNFs), a recent advances material in functional template, are a sustainable resource for templating, can be easily remove through thermal treatment, display high specific surface area, and easy in modification.⁴ Combining Ni nanoparticle with CNFs as template, and after that coating it with Al₂O₃ could prevent Ni sintering, improve diffusion, and enhance activity.

Hence, in this research, Ni nanoparticle encapsulated on $Al_2O_3/SBA-15$ was prepared through a post loading strategy. As comparison with difference catalyst design, Ni nanoparticle coated on $Al_2O_3/CNFs$ was prepared through co-assembly strategy. To more comprehensive study, the difference in molecular Ni precursor use, Ni(acac)₂ as organic and Ni(NO₃)₂ as inorganic was studied as well, including the introduction of CeO₂. The characterization and mechanism of the prepared catalysts are also investigated.

Materials and Methods

Ni#Al₂O₃/SBA-15 catalyst was prepared using the post-loading strategy. Firstly, mesoporous silica (SBA-15) support was pre-synthesized using the triblock copolymer synthesis. Then, the prepared Ni nanoparticle, CeO₂, and Al₂O₃ were loaded into the prepared SBA-15. On the other hand,



Ni@Al₂O₃/CNFs catalyst was prepared using the co-assembly strategy. At the same time, CNFs was prepared using TEMPO oxidation method to reach high carboxylate content. Followed by the loading of Ni nanoparticle, and Al₂O₃ into the CNFs. Both of prepared catalyst types were calcined at 600 ° C for 6 h and molder (290-425 m) at 40 MPa.

Catalytic activity test was conducted through the prepared catalyst loaded into a fixed-bed flow reactor. Firstly, the catalyst underwent pre-treatment, including a 3 h H_2 reduction at 600°C followed by a 2 h steam treatment for passivation. Subsequently, steam reforming of acetic acid was performed. The reaction pressure was 0.1 MPa, and the reaction temperature was 650°C. The gas (GC-TCD) and liquid (GC-FID) products were analyzed.



Figure 1 Steam reforming of acetic acid over prepared catalyst. (a) H_2 yield and (b) carbon product yield. Reaction condition 650 °C, S/C= 3.17, and WHSV= 21 h⁻¹

Fig. 1 reveals H₂ and carbon-based product yield of acetic acid steam reforming using post-loading strategy and co-assembly strategy, respectively. Both of prepared catalyst obtained H_2 yield up to 75%, in term of specific condition (Fig. 1a). To interpret differently of each strategy, firstly- mesoporous hexagonal catalyst design obtained by post loading strategy showed that molecular Ni(acac)₂ precursor received the better activity test than Ni(NO₃)₂ due to a higher number of active Ni nanoparticle sites (proven in H₂-TPR analysis). Further, Ni nanoparticle catalyst (Independently prepared using Ni(acac)₂ precursor) shown the more stability in activity test than the molecular $Ni(acac)_2$ (Fig. 1b). The addition of CeO₂ revealed that the catalyst with 0.1 wt.% of CeO₂ exhibited superior performance of H₂ yield and carbon-based product compared to higher loadings (up to 1 -5 wt.%) (Fig 1ab), confirming that at the optimum loading of CeO_2 could improve the water gas shift reaction in steam reforming. Next, through co-assembly strategy, noncapsular catalyst design, H_2 yield was achieved optimum with 0.2 g CNFs loading compared to other loadings (0.1 and 0.3 g). The addition of hard template, CNFs, impacted the activity test due to the obtained balance of surface area, pore volume and pore diameter (proven by BET analysis). Hence, directly speaking, the steam reforming of acetic acid using Ni nanoparticle encapsulated on CeO₂/Al₂O₃/SBA-15 and Al₂O₃/CNFs prepared catalyst was successfully conducted using a fixed bed flow reactor.

References

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Acknowledgements

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