Factors Influencing Nanoscale Catalysts Prepared Impregnation Method

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Abstract: With the rapid advancement of nanotechnology, nanocatalysts have found extensive applications in chemical reactions and environmental remediation. The impregnation method stands as a pivotal technique for the synthesis of nanocatalysts, with its efficacy influenced by a multitude of factors. This study substantiates that the type and concentration of the impregnating agent significantly impact the catalyst's loading capacity and dispersion. Furthermore, the duration and temperature of impregnation effectively govern the particle size of the catalyst, thereby optimizing its catalytic performance. Additionally, the physicochemical properties of the support, along with the pH and ionic concentration of the solution, collectively alter the reduction behavior of metal ions, further affecting the formation mechanism and overall performance of the catalyst. Future in-depth investigations into the interplay of these factors will pave the way for innovative strategies and methodologies for the efficient fabrication of nanocatalysts. Understanding these complex interdependencies is crucial for designing catalysts with improved selectivity, activity, and stability, which are essential for advancing various catalytic processes and addressing challenges in sustainable chemistry and environmental protection.

Keywords: Impregnation, method, nanokatal.

1. Introduction

In today's field of chemical engineering and materials science engineering, catalytic technology, as an important means, has received more and more widespread attention. The core of catalytic technology lies in catalysts, which can make difficult reactions feasible by providing a reaction path with lower energy. This capability not only increases the reaction rate but also enhances the selectivity of the reaction, resulting in a significant increase in the yield and purity of the target product [1]. With the growing global demand for sustainability and environmentally friendly technologies, catalytic science is facing new challenges and opportunities. The development of new, efficient, and environmentally friendly catalysts, as well as the optimization of existing catalytic processes, has become a common pursuit of chemists and engineers.

As a new type of material, nanomaterials have the characteristics of large specific surface area, excellent catalytic performance, high activity and so on, and have been widely used in the field of catalysis. Compared with traditional catalysts, nano catalysts have a high surface area, which gives them more active sites, which greatly accelerate the reaction process. The preparation methods of catalysts include impregnation method, precipitation method and mixing and kneading method. Among them, impregnation method is one of the important methods to prepare nano catalysts. The core of this method is to evenly penetrate the solution containing active components into the porous carrier, and make the active components evenly dispersed in the pore structure of the carrier through physical or chemical adsorption [2]. It is widely used because of its low cost and simple operation. With the rapid development of materials science and nanotech, the research and development of nano-catalysts have become crucial in chemistry, energy, and environmental engineering. These catalysts' high specific surface area provides more active sites for reactants, and their unique electronic and coordination environments give them extraordinary capabilities in catalytic reactions.

In the preparation of nano-catalysts by impregnation method, solution concentration and impregnation time are key parameters, which affect the loading and dispersion of active components on the carrier. The physical and chemical properties of the carrier, such as pore structure and surface characteristics, play a decisive role in the dispersion and contact of active components. The calcination and reduction conditions further affect the crystal phase structure of the catalyst and the valence state of the active component, thus determining the final performance of the catalyst. In order to optimize the performance of nano-catalysts prepared by impregnation method, this paper aims to study the key influencing factors of this method to prepare nano-catalysts, including solution concentration and impregnation time, carrier properties and catalyst distribution, calcination and reduction conditions, and discusses their effects on catalytic performance.

2. Solution Concentration and Impregnation Time

The concentration of the active component in the precursor solution is directly correlated with the catalyst loading; higher concentrations result in increased loading. In the oxidation reaction of methoxypropanol (MOP) catalyzed by Ag/SiO_2, it was observed that among the four catalysts with varying active component concentrations of 0.2705 g/mL, 0.2925 g/mL, 0.318 g/mL, and 0.3485 g/mL, the Ag/SiO_2 catalyst prepared at 0.3485 g/mL exhibited the highest catalyst loading. Under this optimal loading condition, both the conversion rate of methoxypropanol and the selectivity for methoxypropanone (MOA) were maximized. This enhancement can be attributed to the uniform dispersion of Ag throughout the support at higher loadings, which provides an adequate number of active sites for the reaction [3].

Moreover, extending the impregnation time generally improves the uniformity and efficiency of the catalyst loading. However, excessive impregnation time may diminish the uniformity of the catalyst loading. By maintaining a controlled active component drying time of 6 hours, an impregnation period of 4 h, and an impregnation temperature of 60 °C, a series of honeycomb-like VPO catalysts were synthesized with varying impregnation times of 2, 4, 6, and 8 hours to evaluate the effect of impregnation time on the VPO catalytic reduction of NOx. The experimental results indicated that as the impregnation time increased from 2 hours to 4 hours, the catalyst's denitration efficiency improved when tested within the temperature range of 180 – 240 °C, achieving a remarkable 99% denitration efficiency at 240 °C with the 4-hour catalyst. However, with further extension of the impregnation time, the catalytic activity began to decline; at 8 hours of impregnation, the denitration efficiency at 150 °C fell below 60%. Thus, the optimal impregnation time during the formation process is concluded to be 4 hours. This is attributed to the fact that longer impregnation times allow the active components sufficient opportunity to penetrate the internal pores of the support, while excessive durations may lead to the aggregation of active components on the support's surface, thereby compromising loading uniformity [4].

Within a specific range, an increase in pH value can lead to a reduction in the oversaturation of the coprecipitation system, slowing down the rate of crystal nucleation while accelerating crystal growth, thus affecting the particle size and morphology of the precursor. An analysis of XPS spectra regarding O1s on the Ce-W-Ti catalysts at different pH values—pH = 1.5 (S1), pH = 7 (S2), pH = 9 (S3), and pH = 11 (S4)—reveals that as pH increases, the ratio of Oα/Oβ rises, while the ratio of Ce^{3+}/Ce^{4+} initially increases and then decreases.

Temperature also significantly influences the adsorption process, typically manifested as a reduction in the amount of adsorbate adsorbed on the adsorbent with increasing adsorption temperature, under the same partial pressure of the adsorbate. In the oxidation reaction of methoxypropanol catalyzed by Ag/SiO_2, a comparative study among five temperatures (260 °C, 280 °C, 300 °C, 320 °C, and 340 °C) indicates that as the temperature rises, the selectivity for MOA decreases while the selectivity for the byproduct acetone (AC) [5].

3. Additives

The incorporation of additives, as opposed to utilizing the catalyst in isolation, can significantly enhance catalytic performance by improving dispersion, thus markedly increasing experimental efficiency. In the preparation of hydrogenation catalysts for polycyclic aromatic hydrocarbons, it was observed that the use of nickel and nickel-cerium formulations to create granular γ-Al_2O_3 support catalysts led to an increase in the specific surface area following a single saturation impregnation of γ-Al2O3. This enhancement is attributed to the dispersive effect of the additives, which facilitates the uniform distribution of nickel species across the support surface. The presence of cerium, in particular, contributes to the effective dispersion of the catalyst's active components. This occurs as additives modify the specific surface area of the catalyst, promoting a more even distribution of the active components on the support, thereby augmenting both dispersion and catalytic performance [6].

In the context of research on the heterogeneous catalytic hydrogenation of nitrile rubber, considerable attention was given to the influence and alteration of electronic structure by the additives. In this study, various additives such as sodium, calcium, scandium, titanium, vanadium, boron, aluminum, and zirconium—were introduced into a palladium-based catalyst as the active component. The findings revealed that irrespective of the method of zirconium addition, it effectively diminishes the size of palladium nanoparticles, resulting in smaller, more dispersed particles on the support. Furthermore, the incorporation of zirconium alters the electronic structure of palladium, increasing its electron density and placing it in a state rich in electrons, which significantly benefits the adsorption and activation of double bonds, as well as the adsorption and dissociation of hydrogen gas [7]. This series of experiments sufficiently illustrates that the presence of additives aids in modulating the electronic density of the active components, influencing their interactions with the support, and promoting a more homogeneous distribution of the active components, ultimately resulting in smaller particle sizes improved dispersion.

4. Calcination and Reduction

The calcination temperature plays a crucial role in determining the structure and activity of catalysts. For instance, it affects the specific surface area, porosity, and surface properties of the catalyst. Similarly, the duration of calcination significantly influences catalyst performance. Insufficient calcination time may lead to incomplete decomposition of the precursor, while excessive calcination can result in sintering of the catalyst. For example, a study utilizing nitrogen physisorption to investigate the mechanism of calcination temperature's effect on Cu/ZSM-5 catalysts found that when the calcination temperature ranged from 180 to 300 °C, the catalyst achieved over 95% denitration efficiency. At a calcination temperature of 500 °C, the catalyst exhibited maximum catalytic activity, with a specific surface area of 299 m^2/g and a well-developed porous structure. However, at calcination temperatures of 600 or 700 °C, sintering phenomena occurred on the catalyst surface, resulting in a decrease in specific surface area to below 125 m^2/g and a subsequent reduction in catalytic activity [8]. Moreover, the temperature and duration of the calcination process have a significant impact on the transformation of the precursor and the crystalline phase structure of the catalyst. An optimal calcination temperature can facilitate the complete conversion of the catalyst precursor, yielding the desired catalytic phase. For example, in MnOx/ZSM-5 catalysts, at a calcination temperature of 550 °C, Mn_2O_3 emerged as the predominant crystalline phase on the catalyst surface.

Simultaneously, the use of various gases during pretreatment can also affect catalyst performance, with the reducing atmosphere capable of enhancing catalytic activity to some extent. For instance, pretreating nanosilica with CO and H2 resulted in significantly improved catalytic activity. This improvement is attributed to CO altering the crystalline phase of the catalyst and generating a substantial amount of hexagonal cobalt crystalline phase, which is beneficial for enhancing the activity of Fischer-Tropsch synthesis, while the introduction of H2 helps to eliminate part of the carbon deposition [9].

Additionally, different reduction temperatures and durations can also impact the catalyst's activity. In studies involving SiO_2 catalysts for Fischer-Tropsch synthesis reactions, it was observed that extending the reduction time at a temperature of 240 °C or increasing the reduction temperature to 270 °C both facilitated the reduction of the catalyst.

To enhance the performance of nanoscale oxidants, it is imperative to carefully control the calcination temperature and duration during the preparation of nanoscale catalysts via impregnation methods. Higher calcination temperatures promote increased crystallinity and growth of metal particles; however, excessively high temperatures may lead to particle agglomeration, thereby diminishing activity. Proper control of calcination time ensures complete decomposition of the precursor and appropriate crystallization of the catalyst [10]. Furthermore, managing the reducing atmosphere (Hydrogen, CO) and reduction temperature is essential to achieve optimal metal dispersion and electronic properties of the catalyst. Adequate reduction conditions can facilitate the reduction of metal particles and the formation of the active phase, thereby enhancing both the activity and stability of catalyst.

5. Conclusion

This study, through an analysis of the factors influencing the preparation of nanoscale catalysts via the impregnation method, has demonstrated that optimizing the selection and concentration of the impregnating agent, as well as the impregnation time and temperature, the physicochemical properties of the support, and the pH and ionic concentration of the solution, can significantly enhance the catalytic performance of nanoscale catalysts and control the size of metal particles. This, in turn, improves their surface activity and catalytic efficiency. Future research should further investigate the intricate relationships among these factors to advance the development and application of high-performance nanoscale catalysts.

Authors Contribution

All the authors contributed equally and their names were listed in alphabetical order.

References

[1] *Yu, Z., Yurong, Z., & Shaoqi, M. (2024). Ag/SiO2 catalyst for methoxypropyl alcohol oxidation reaction. Fine Chemicals, https://doi.org/10.13550/j.jxhg.20240150.*

[2] *Yingchun, T., Yongli, P., & Yiyun, Y. (2021). Experimental Study of Immersion Method of Honeycomb VPO Low Temperature Denitration Catalyst. Journal. of Anhui University of Technology (Natural Science), 38(3), 275-281. https://doi.org/10.3969/j.issn.1671-7872.2021.03.007.*

[3] *Chao, Z., Yang, Z., & Jia, X. (2020). The effect of pH value on the preparation of Ce-W-Ti denitration catalyst by impregnation method. Chinese Rare Earths, 41(5), 59-69 https://doi.org/10. 16533 / J.CNKI.15-1099 / TF. 20200031.*

[4] *Ferullo, R. M., Zubieta, C. E., & Belelli, P. G. (2019). Hydrogenated polycyclic aromatic hydrocarbons (HnPAHs) as catalysts for hydrogenation reactions in the interstellar medium: a quantum chemical model. Physical Chemistry Chemical Physics: PCCP, 21(22), 1212–122. https://doi.org/10.1039/c9cp02329a.*

[5] *Liang, H., Zhang, G., Li, Z., Zhang, Y., & Fu, P. (2023). Catalytic hydrogenation of CO2 to methanol over Cu-based catalysts: Active sites profiling and regulation strategy as well as reaction pathway exploration. Fuel Processing Technology, 252, 107995-. https://doi.org/10.1016/j.fuproc.2023.107995.*

[6] *Wei, L., Zhiquan, T., & Jie, L. (2006). Low-temperature selective catalytic reduction of NO with NH3 over Ce-Mn/TiO2 catalyst Ce-Mn/TiO2. Journal of Environmental Science, 26(8), 1240-1245. https://doi.org/10.3321/j.issn: 0253-2468.2006.08.003.*

[7] *Yaxi, W., Shuzheng, W., & Hongwei, Z. (2022). Research Progress on Heterogeneous Catalytic Hydrogenation of Nitrile Butadiene Rubber. Chemical Progress, 41(09), 4790-4800. https://doi.org/10.16085/j.issn.1000-6613.2021-2323.*

[8] *Zhizhou, W., Yiding, G., & Binghong, L. (2019). Effect of calcination temperature on catalytic activity of Cu/ZSM5 catalyst. Coal Science and Technology, 47(11), 206-210. https://doi.org/10.13199/j.cnki.cst.2019.11.029.*

[9] *Xiaochu, Y. (2018). Study on the effect of calcination temperature on the catalytic oxidation performance of MnOx/ ZSM-5. Thermal Power Engineering, 33(4), 56-62. https://doi.org/10.16146/j.cnki.rndlgc.2018.04.009.*

[10] *Wu, H., Chen, T., Wu, J., Pao, C., & Chen, C. (2021). Influence of sodium-modified Ni/SiO2 catalysts on the tunable selectivity of CO2 hydrogenation: Effect of the CH4 selectivity, reaction pathway and mechanism on the catalytic reaction. Journal of Colloid and Interface Science, 586, 514–527. https://doi.org/10.1016/j.jcis.2020.10.117.*