Supported metal nanoparticles on hierarchically porous carbons derived from metal-modified metal-organic frameworks

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Introduction

The global demand for fuels and chemicals derived from sustainable and abundant sources (i.e., lignocellulosic biomass) has triggered the development of heterogeneous catalysts capable of handling these diverse feedstocks [1]. To attain high catalyst activity and high selectivity to desired products, the heterogeneous catalyst should be stable in aqueous media, have a high surface area and high dispersion of active metals, have a high mesoporosity for facilitating the diffusion of large biomass derivatives/intermediates to the active sites, and contain the desirable phases of active metals [2].

In this study, we used metal-modified IRMOF-3 (M/IRMOF-3), prepared via post-synthetic modification (PSM), as the initial template/carbon precursor to the catalytic material. When subjected to carbonization and carbothermal reduction (CCR) at 1000 °C, metal nanoparticles supported on nanoporous carbon (M/NC3) were synthesized (Figure 1a) [2,3]. Ru, W, V, and Ti were selected due to their reported activity for the conversion of biomass model compounds (e.g., levulinic acid (LA) and benzyl alcohol) [1]. The properties and catalytic performance of the synthesized M/NC3 materials were compared with those of M/NC1 with similar metal loadings. These were prepared from the CCR of metal-impregnated (IMP) IRMOF-1 (M/IRMOF-1) under the identical condition as that to prepare M/NC3 materials (Figure 1b) [2].

Materials and Methods

Procedures for synthesis of materials, evaluation of catalytic performance, and characterizations were specifically described in the ‘Experimental’ section of [2].

Results and Discussion

The use of transition metal-modified metal-organic frameworks through post-synthetic modification as the carbon precursor and template during CCR was expected to minimize the aggregation of metal nanoparticles during CCR by isolating the various transition metals from one another on the M/IRMOF-3 materials. HRTEM images obtained on M/NC3 materials showed much smaller particle sizes (3.9-6.5 nm) relative to those derived from M/IRMOF-1 (12.2-13.9 nm) (where IRMOF-1 does not contain reactive amine sites for the coordination of metal precursors) [2].

Interestingly, the carbothermally reduced M/IRMOF-3 materials could be used to target the final resulting metal phase, such as oxide phases, metallic phases for Ru and carbide phases from other transition metals (i.e., W, V, and Ti) [2]. Furthermore, the formation of Ru nanoparticles with no encapsulation by a carbon shell, and the formation of unique WC1-X nanoparticles with enhanced thermal stability were observed using this method [2].

The resulting M/NC materials were applied as catalysts for the liquid-phase conversion of lignocellulosic biomass model compounds to form various value-added chemicals [2]. Levulinic acid served as a model compound for its conversion to γ-valerolactone and methyl levulinate, whereas benzyl alcohol served as a model compound of lignin for its conversion to benzaldehyde. The M/NC3 materials showed enhanced catalytic properties compared to those of the corresponding M/NC1 materials [2]. This presentation will highlight the synthesis and catalytic properties of these interesting materials derived from post-synthetically modified metal-organic frameworks.

Significance

This study successfully demonstrates the adaptability of the CCR method using transition metal post-synthetically modified MOFs to control the properties of highly efficient M/NC catalysts for various lignocellulosic biomass conversion reactions.

References