Selective hydrogenation of 5-hydroxymethylfurfural to biofuel 2,5-dimethylfuran over CuNi/ZrO_2-SBA-15 catalyst

Ningmeng Hu[a], Guowen Li[b, c], Zhengyang Duan,[a] Lei Tao[d, *]

a. College of Resources, Environment and Chemistry, Chuxiong Normal University, Chuxiong 675000, PR China

b. Ecological and Environmental Monitoring Station of DEEY in Yuxi, Yuxi 653100, PR China

c. Plateau Lake Station of Fuxian Lake Wetland in Yunnan, Yuxi 653100, PR China

d. College of Resources and Environment, Anqing Normal University, Anqing 246133, PR China

Preparation of the Carrier SBA-15

First, 4 g of P123 was dissolved as a structural directing agent in a beaker containing 120 mL of (2 M) hydrochloric acid and 30 mL of deionized water. The mixture was continuously stirred in a water bath at 40 ℃ until P123 was completely dissolved. After 4 h, 9.6 g of tetraethyl orthosilicate (TEOS) was added dropwise, acting as the silicon source, with stirring maintained for a further 12 h. Then, 2 g of glucose was slowly added to the mixture, and the resulting solution was continuously stirred at 40 ℃ for another 12 h. Thereafter, the mixture was transferred into a Teflon-lined reactor and subjected to a 24-h crystallization process at 120 °C. Then, the reactor was removed and cooled to room temperature. The resulting white solid was filtered and washed with deionized water on multiple occasions until the pH of the solution reached a neutral state, thereby removing the residual hydrochloric acid from the mixture. Then, the filtered sample was subjected to an overnight drying process in an oven maintained at 80 °C. Finally, the sample was heated in a muffle furnace at a rate of 3 ℃/min to 500 ℃ and maintained for 6 h. The resulting sample was identified as the carrier SBA-15.

Preparation of ZrO_2

ZrO_2 was prepared as follows: A solution of 2.0 mol/L zirconium oxynitrate was prepared by diluting nitric acid. Then, a solution of 4.0 mol/L sodium hydroxide was slowly added to this solution. The mixture

was continuously stirred at room temperature for 30 min. The resulting mixture was filtered and washed with deionized water multiple times until the pH reached approximately 7. Then, the samples were dried at 110 ℃ for 12 h. Finally, the sample was heated in a muffle furnace at a rate of 15 ℃/min to 500 ℃ and maintained for 6 h, resulting in the formation of ZrO_2.

Preparation of ZrO_2/SBA-15

The ZrO_2/SBA-15 was prepared via an equivalent-volume impregnation method. The typical procedure involved the addition of 0.8 g of SBA-15 and 0.2 g of ZrO_2 to a beaker, which was then continuously stirred at 60 °C for 2 h and subsequently at 70 °C for 2 h. Thereafter, the mixture was dried overnight in an oven at 80 °C. Subsequently, the sample was reduced in a muffle furnace at a rate of 2 °C /min to 350 °C and maintained for 5 h under a H_2 flow velocity of 60 mL/min.

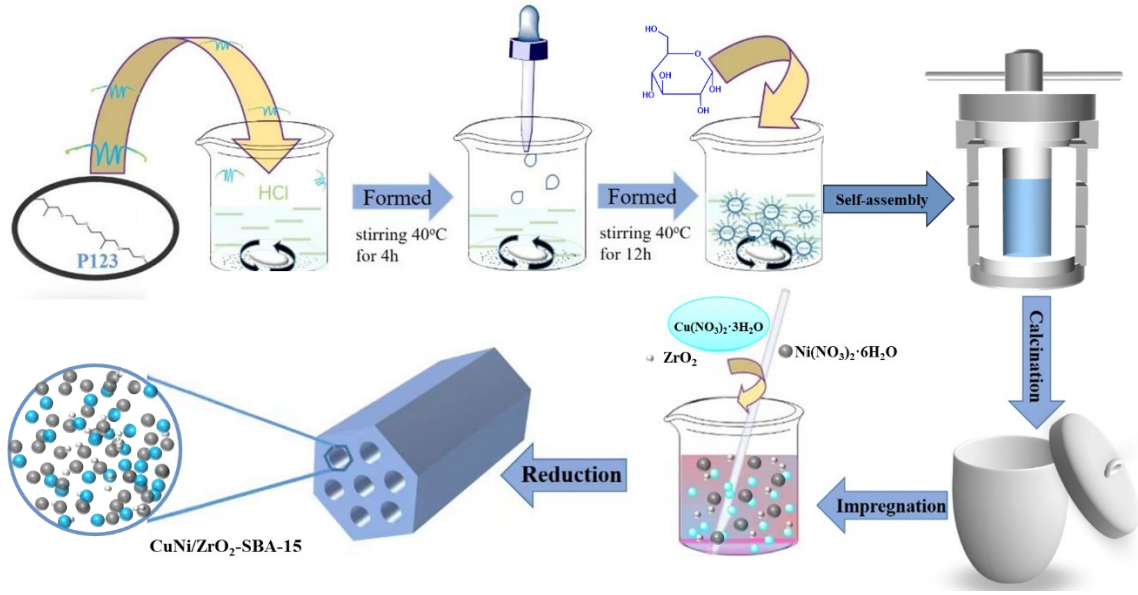

Fig. S1 Schematic illustration of the synthesis of CuNi/ZrO_2-SBA-15 catalyst

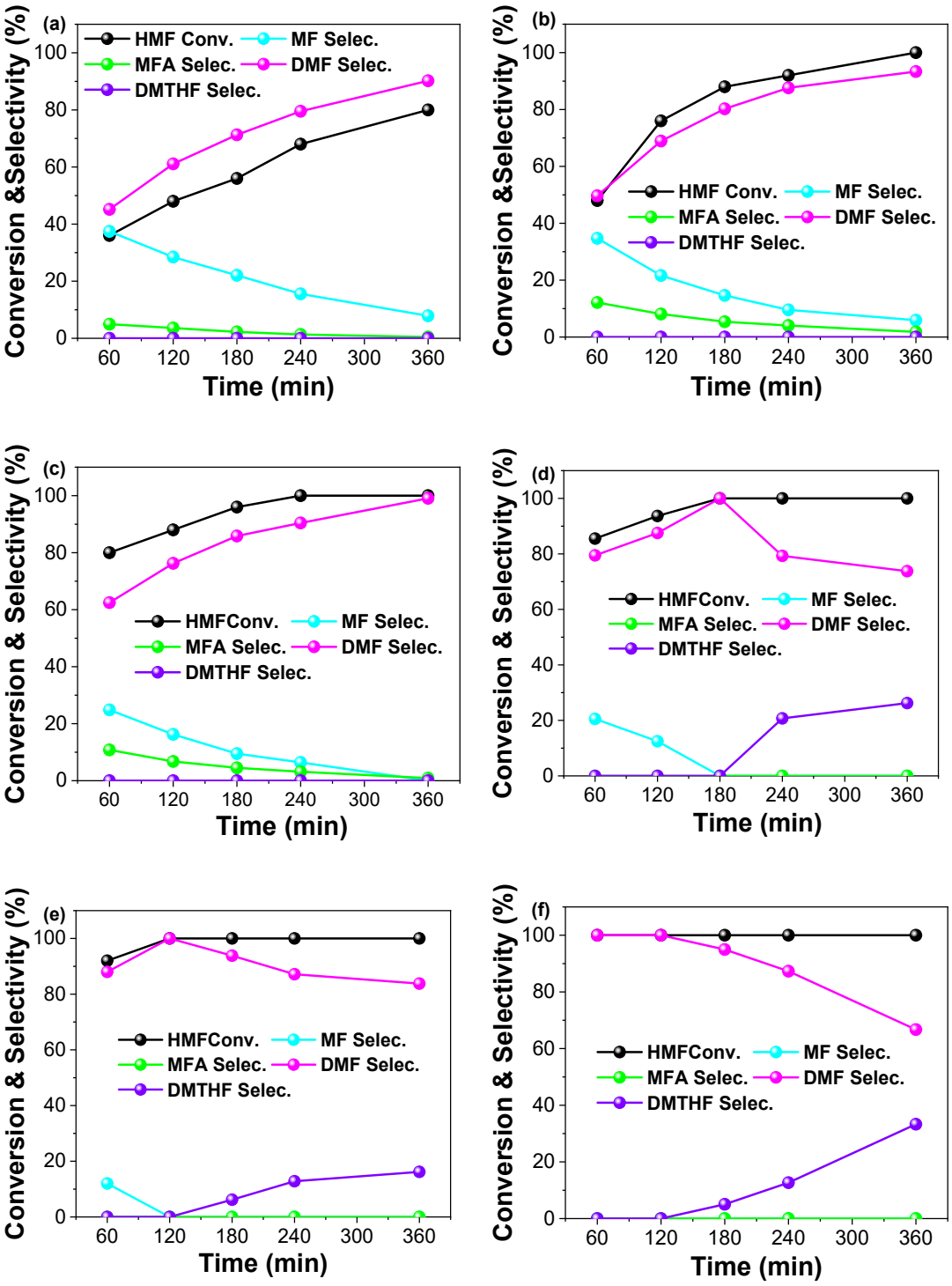

Fig. S2. Effect of temperature and time on the hydrogenation of HMF, (a) 150 ℃, (b) 160 ℃, (c) 170 ℃, (d) 180 ℃, (e) 190 ℃, (f) 200 ℃. Reaction conditions: 50 mg HMF, 116 μL isopropanol, 25 mg catalyst, 2 MPa H_2.

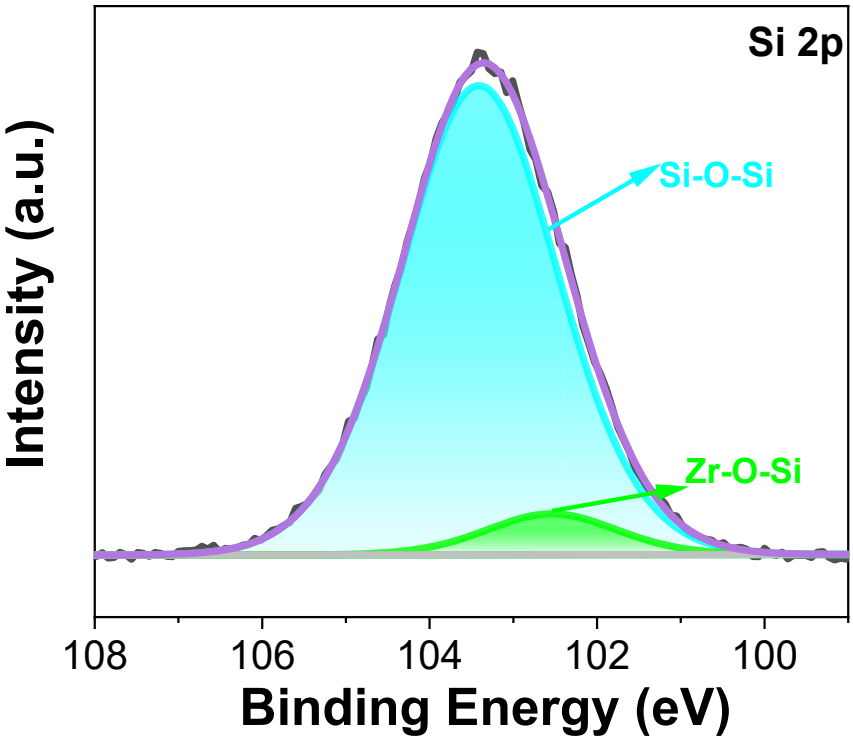

Fig. S3 XPS spectra of Si 2p for CuNi/ZrO_2-SBA-15 catalyst

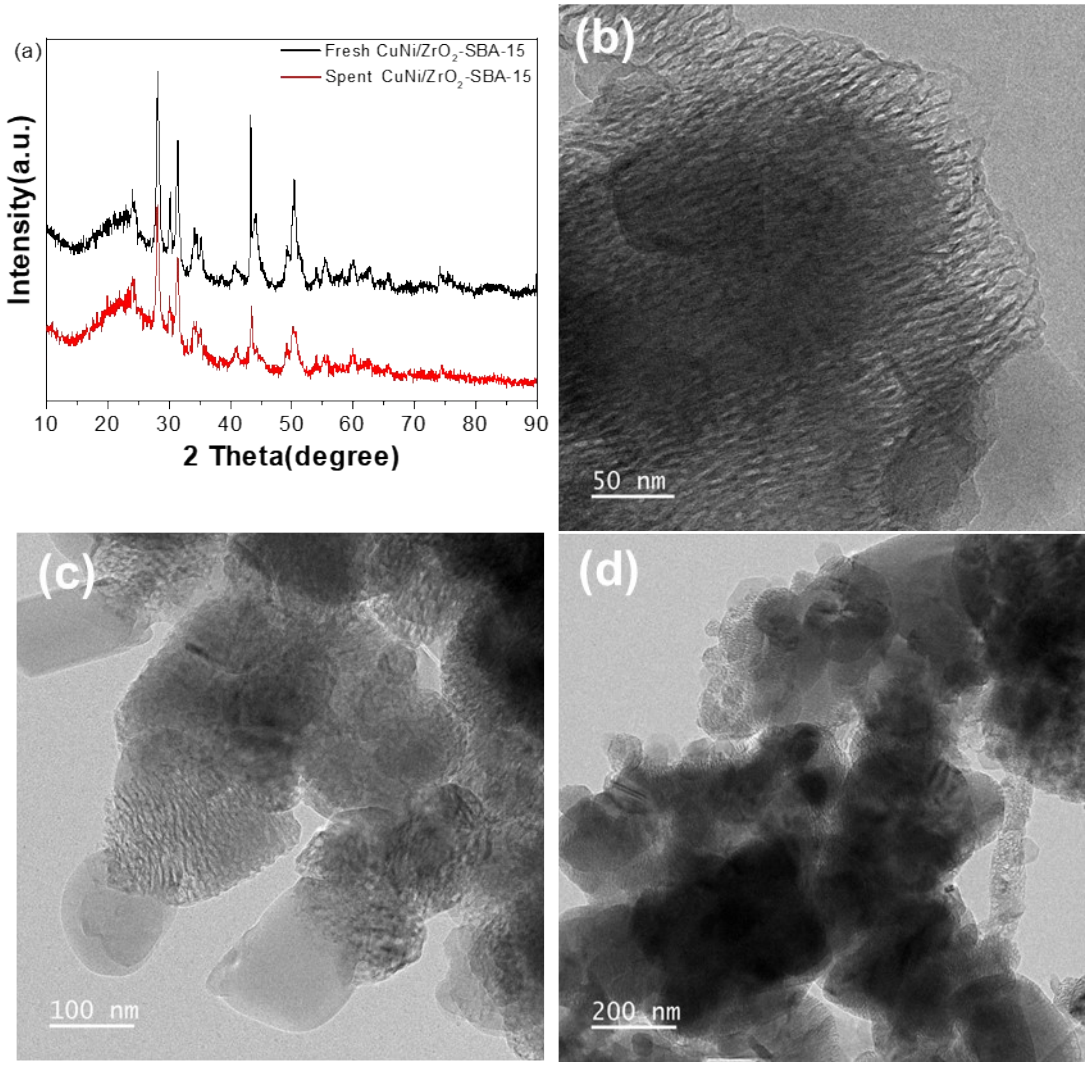

Fig. S4 (a) XRD patterns of fresh and spent CuNi/ZrO_2-SBA-15, (b-d) TEM images of spent CuNi/ZrO_2-SBA-15.

Table S1 Comparasion of HMF conversion and DMF selectivity of catalyst

Catalyst	Condition	HMF conversion	DMF selectivity	Reference
Fe-Pd/C	150 °C, 20 bar H_2, 2 h	100%	88%	Abhijit D. Talpade et al, 2019
CoNCx/NiFeO	180 °C, 1 MPa H_2, 6 h	99.8%	94.3%	Xia et al, 2022
Ni/TMC	180 °C, 3 MPa H_2, 3 h	100%	97.6%	Huang et al, 2025
Co_2Ni_1@N_1C-700	150 °C, 1 MPa H_2, 3 h	100%	98.9%	Liao et al, 2025
CuNi/ZrO_2-SBA-15	180 °C, 2 MPa H_2, 3 h	100%	100%	This work

Reference

[1] Abhijit D. Talpade, Manishkumar S. Tiwari, Ganapati D. YadavSelective hydrogenation of bio-based 5-hydroxymethyl furfural to 2,5-dimethylfuran over magnetically separable Fe-Pd/C bimetallic nanocatalyst[J]. Molecular Catalysis, 2019, 465: 1-15.

[2] Jing Xia, De Gao, Feng Han, Yan Li, Geoffrey I. N. Waterhouse, Efficient and Selective hydrogenation of 5-hydroxymethylfurfural to 2,5-Dimethylfuran over a non-noble CoNCx/NiFeO Catalyst[J]. Catalysis Letters, 2022, 152: 3400-3413.

[3] Rulu Huang, Jianchun Jiang, Jie Liang, Shanyong Wang, Yuwei Chen, Xianhai Zeng, Kui Wang. Selective hydrogenation of 5-hydroxymethylfurfural triggered by a high Lewis acidic Ni-based transition metal carbide catalyst[J]. Green Energy & Environment, 2025, 10(3): 573-584.

[4] Xiaoqing Liao, Haishuai Cui, Hean Luo, Yang Lv, Pingle Liu. Highly efficient selective hydrodeoxygenation of 5-hydroxymethylfurfural to 2,5-dimethylfuran over Co-Ni in-situ encapsulated in biochar-based carbon catalysts: The crucial role of CoNi alloys and Co-Nx species[J]. Chemical Engineering Journal, 2025, 503: 158336.