Synthesis of Bulk and Supported Molybdenum Carbide by a Single-Step Thermal Carburization Method

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Supporting Information

Preparation of 23 wt % β -Mo₂C/ γ -Al₂O₃ by the TPre method

The MoO₃/ γ -Al₂O₃ precursors were prepared by impregnation of γ -Al₂O₃ using aqueous solutions of (NH₄)₆Mo₇O₂₄·4H₂O, followed by airing overnight, drying for 3 h at 120 °C, and calcinations at 500 °C for 5 h in air. The MoO₃/MCM41 precursor was carburized under 20 % CH₄/H₂ (v/v) mixture at a VHSV (volume hourly space velocity) of 6000 h⁻¹. The temperature of the carburization process was firstly increased at room temperature to 500 °C at the rate of 10 °C/min. Subsequently, the carburization was operated by the ramping rate of 1 °C/min from 500 °C to 700 °C, and kept at the final temperature for 1.5 h. The system was cooled to room temperature in H₂ flow and passivated overnight in flowing 1% O₂/N₂ (v/v) gas to avoid strong bulk oxidation. The β -Mo₂C/ γ -Al₂O₃ catalyst with theoretical loadings of 23 wt % β -Mo₂C was prepared.

Preparation of 23 wt % γ -Mo₂N/ γ -Al₂O₃ by the HMT-based method

The alumina-supported salt precursor was prepared by impregnation of γ -Al₂O₃ with an aqueous solution of (NH₄)₆Mo₇O₂₄·4H₂O and HMT with a fixed mole ratio 1:2, which was obtained by dissolving the reagents in 15% NH₃·H₂O solution. The sample was then dried naturally for 48 h and dried at 80 °C for 6 h. The precursor was heated at a rate of 10 °C min⁻¹ and kept at 650 °C for 2 h under a flow of argon. The product was cooled to room temperature under argon and passivated in a flow of 1% (v/v) O₂/N₂. The γ -Mo₂N/ γ -Al₂O₃ catalyst with theoretical loadings of 23 wt % γ -Mo₂N was prepared.

Preparation of 23 wt % γ -Mo₂N/ γ -Al₂O₃ by the TPR method

The $\text{MoO}_3/\gamma\text{-Al}_2\text{O}_3$ precursors were prepared by impregnation of $\gamma\text{-Al}_2\text{O}_3$ using aqueous solutions of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$, followed by airing overnight, drying for 3 h at 120 °C, and calcinations at 500 °C for 5 h in air. The $\text{MoO}_3/\gamma\text{-Al}_2\text{O}_3$ precursor was then nitrided to yield $\text{Mo}_2\text{N}/\gamma\text{-Al}_2\text{O}_3$ catalyst. The flowing ammonia had a VHSV of 6000 h⁻¹. The temperature was increased in two steps: rapidly from room temperature to 350 °C (at 6 °C/min), and then slowly from 350 to 650 °C (at 1 °C/min). The temperature was then held at 650 °C for 2 h. The system was then cooled to room temperature in flowing NH_3 , and passivated overnight in flowing 1% O_2/N_2 (v/v) gas to avoid strong bulk oxidation. The $\gamma\text{-Mo}_2\text{N}/\gamma\text{-Al}_2\text{O}_3$ catalyst with theoretical loadings of 23 wt % $\gamma\text{-Mo}_2\text{N}$ was prepared.