

Early Transition Metal Carbide and Nitride Catalysts for Fischer-Tropsch Synthesis

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Introduction

Dwindling crude oil resources and increased awareness of the impact of carbon emissions encourage the development of processes and materials to convert renewable resources into liquid transportation fuels and chemical feedstocks. The production of liquid hydrocarbon fuels from biomass-derived synthesis gas via Fischer-Tropsch synthesis (FTS) has emerged as a promising route, producing fuels with very low aromaticity and virtually zero sulfur content. In order to improve the feasibility of this process, FTS catalysts with enhanced activities and selectivities towards valuable products such as C₂-C₄ hydrocarbons, gasoline, and diesel need to be demonstrated.

Early transition metal carbides and nitrides are a promising class of materials for use as FTS catalysts [1, 2]. Previous efforts have shown that Mo₂C produces mainly light hydrocarbons [3] and has stable activities for H₂:CO ratios ranging from 1:1 to 3:1 [2]. These materials also possess properties similar to those of platinum-group metals [4, 5], and are sulfur tolerant [6]. Moreover, transition metal carbides and nitrides can be synthesized with high surface areas ranging up to 200 m²/g [7]. The objectives of this work are to determine the FTS activities and selectivities of Group V and VI carbides and nitrides and to investigate the mechanisms over these catalysts.

Materials and Methods

A series of high surface area Group V and VI transition metal carbides and nitrides (Mo₂C, Mo₂N, VC, VN, NbC, NbN, W₂C, and W₂N) was synthesized via temperature programmed reaction of the parent metal oxide with either 15% CH₄/H₂ or NH₃. Phase analysis of these materials was performed by X-ray diffraction using a Rigaku Miniflex diffractometer operating with Cu K_α radiation. The surface areas were determined via N₂ physisorption at 77K using a Micromeritics ASAP 2010 analyzer. Surface morphologies of these materials were studied using a Philips XL-30 field emission gun scanning electron microscope.

The FTS performance characteristics were evaluated using 100-200 mg of catalyst supported on a quartz wool plug in a stainless steel U-tube reactor enclosed in an electric furnace. The reactions were carried under the following conditions: 2:1 H₂:CO, 200-250°C, 25 bar, and GHSV = 9600 – 42000 h⁻¹. Effluent gas composition was analyzed using a Varian gas chromatograph equipped with thermal conductivity and flame ionization detectors. Two commercial catalysts (Fe and Co) were used to benchmark performance.

Results and Discussion

All of the carbide and nitride catalysts were active for FTS; however, the V, Nb, and W carbides and nitrides were much less active than the Mo₂C and Mo₂N catalysts.

Gravimetric CO consumption rates for the Mo₂C and Mo₂N catalysts are compared to those for the Fe and Co commercial catalysts in Figure 1. For Mo₂C and Mo₂N, approximately 21%, 11%, and 20% of the CO was converted to CH₄, C₂, and C₃+ hydrocarbons respectively, compared to 44%, 4%, and 42% for the Co catalyst. Approximately 40% of the CO was converted into CO₂ over Mo₂C and Mo₂N, presumably due to their high water gas shift activities, and ~6% was converted to methanol. The Fe catalyst showed very similar selectivities to the Mo₂C and Mo₂N catalysts. The Co catalyst did not appear to be as active for the water gas shift and did not form methanol. Some degree of water gas shift activity could be useful for adjusting the H₂:CO ratio of biomass-derived synthesis gas (H₂:CO = 0.8 – 1.2) to a more usable range.

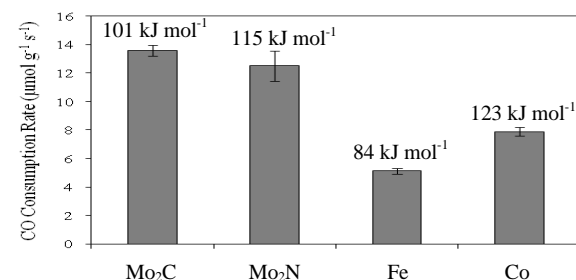


Figure 1. Gravimetric CO consumption rates and activation energies for FTS over Mo₂C, Mo₂N, Fe and Co catalysts at 230 °C, 25 bar, H₂:CO 2:1, and GHSV = 9600 – 42000h⁻¹.

When fitting the product distributions to the Anderson-Schulz-Flory model, α values for the catalysts were as follows: 0.62 for Co, 0.52 for Fe, and 0.43 for Mo₂C and Mo₂N. This result indicates that Mo₂C and Mo₂N catalysts favored shorter chain hydrocarbons as compared to the commercial catalysts. Moreover, the Fe and Co commercial catalysts produced a higher olefin-to-paraffin molar ratio for any given carbon number than did Mo₂C and Mo₂N.

Significance

Fischer-Tropsch synthesis has traditionally been catalyzed using oxide-supported Fe and Co catalysts. There is a need for catalysts with higher activities and selectivities. Early transition metal carbides and nitrides have been demonstrated to be viable materials for further investigation and could facilitate the commercialization of biomass-to-liquids processes.

References

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