

Fischer-Tropsch synthesis by Nb₂O₅-supported iron or cobalt catalysts

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Introduction

Natural gas and biomass has been becoming more attractive as an energy source due to the constant oil barrel price increasing, and to environment reasons. The Fischer-Tropsch (F-T) synthesis is one way to upgrading them to higher hydrocarbons fuels, and the unique industrial process available nowadays. Soares et al.[1] showed that glycerol could be cleanly converted to synthesis gas (CO/H₂) at temperatures from 498 to 620 K, which allow us to an efficient heat integration with subsequent reactions of this bio-syngas to liquid fuel by F-T synthesis. Simonetti et al.[2] obtained a liquid fuel in the gasoline range by coupling the glycerol reforming and the F-T synthesis using Pt-Re/C and Ru/TiO₂ as the reforming and the F-T catalysts, respectively.

The niobia-supported cobalt [3] catalysts as well as the titania-supported ones [4] showed a higher selectivity toward saturated hydrocarbons in the F-T synthesis compared to the alumina supports, after reduction at high temperatures. Nevertheless, there isn't almost any work reported in the literature related to iron and ruthenium supported on niobia. Then, the aim of this work is to investigate the performance of some Nb₂O₅-supported based catalysts in the F-T synthesis.

Materials and Methods

Catalysts with different cobalt loadings were prepared by the incipient wetness impregnation from a cobalt or iron nitrate, and ruthenium nitrosyl on Nb₂O₅ obtained after calcination of niobic acid HY-340 (CBMM) at 773 K. The catalyst were calcined at 673 K and then, reduced at 773 K.

UV-Vis. Diffuse Reflectance Spectroscopy and Temperature Programmed Reduction were used to characterize the calcined samples.

After reduction the temperature-programmed surface reaction (TPSR) of hydrogen and desorption (CO-TPD) with adsorbed CO experiments were performed in order to investigate the sites' nature. The reactions were accomplished in a fixed or slurry bed at different reactions conditions.

Results and Discussion

The catalysts exhibit high conversion and good stability after several hours time-on-stream. The selectivity toward long hydrocarbons chain, S_{C₅+}, exhibits also a high value, denoting that cobalt supported on niobia may be used as a high-temperature Fischer-Tropsch-based catalyst. It is remarkable that most of the hydrocarbons formed are situated in the range of liquid fuels, C₅-C₁₁ (gasoline and naphtha) and/or C₁₁-C₂₀ (diesel). Negligible amount of waxes (C₂₀+) were formed, thereby enabling to reduce the F-T costs by eliminating the hydrocracking step.

It has been reported that after high temperature reduction, different cobalt species are formed in the interface of Co_x-NbO_y, which are responsible for the long hydrocarbon chain formation. Moreover, these sites have shown high resistance to be destroyed under oxidised condition, as it is during the reaction when large amount with water is produced.

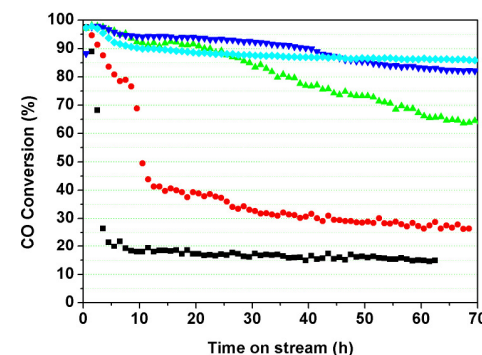


Figure 1. F-T.S. performance of Co/Nb₂O₅ catalyst at different temperatures 200 (■), 220 (●), 250 (▲), 275 (▼), e 300 °C (◆). – CO conversion.

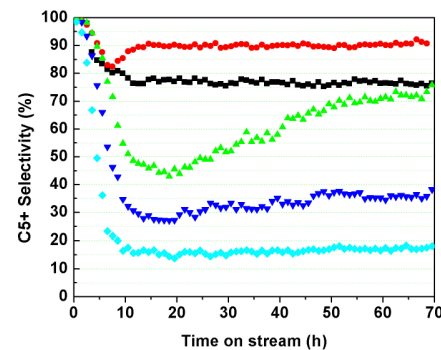


Figure 2. F-T.S. performance of Co/Nb₂O₅ catalyst at different temperatures 200 (■), 220 (●), 250 (▲), 275 (▼), e 300 °C (◆). – C₅+ selectivity.

Conclusions

The catalysts exhibit high conversion and good stability after several hours time-on-stream. The Co/Nb₂O₅ catalyst presented high stability within few hours of reaction, little

selectivity for methane and CO₂, and high selectivity for C₅+, especially for gasoline (C₅ – C₁₁) and diesel (C₁₂ – C₂₀). The ASF parameter calculated values were all greater than 0.75.

The Fe/Nb₂O₅ catalyst presented high activity and stability within few hours of reaction, high selectivity for light hydrocarbons (C₃ – C₁₁).

The TPSR studies provided evidences for the existence of different kinds of sites and/or reaction states after the catalysts were submitted to different pre-treatments.

References

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