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Kinetics of methanation from carbon dioxide and hydrogen using a novel Ni-Co catalyst

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Highlights

- Novel Ni-Co supported on alumina catalysts with different amounts of nickel and cobalt were prepared and characterized,
- The novel catalysts were used for CO_2 methanation under partial vacuum,
- An optimum nickel-cobalt mass ratio was identified based on the methanation catalyst activity and methane selectivity
- A kinetic study was achieved and an heterogeneous kinetic model of Langmuir is proposed

1. Introduction

The continuous increase in global energy consumption and the excessive use of fossil fuels cause continuous increase in CO_2 concentration in the atmosphere which is affecting our planet. It is actually the main cause of the increase in earth's temperature and climate changes by the greenhouse effect. This has pushed the investigations to develop more processes of CO_2 utilization as feedstock to produce fuels and chemicals [1].

The development of renewable energy production as solar and wind turbines, which mismatches the load demand due to its dependence to weather, find in water electrolysis a technically and economically realizable way to store the electric energy produced in form of hydrogen, known as *power-to-gas* concept [2].

Methanation of CO_2 is a promising process bringing an answer to the first mentioned problematic and linked to the second. It consists in using hydrogen produced by water electrolysis in order to transform CO_2 into methane. The methanation reaction is as following:

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O \qquad \Delta H_{298\,k} = -164\ KJ/mol$$

In fact, this leads to an improvement in energy density, the energy density of methane is 40 MJ/m^3 whereas for hydrogen it is 12.7 MJ/m^3. In terms of greenhouse gas emissions, natural gas of which methane is the major constituent and which is the world's third-most-consumed source of energy, is the cleanest of the fuels currently used. In addition, contrary to hydrogen which is very difficult to manipulate due to high risk levels, methane can be directly injected into natural gas pipelines or it can be used as a feedstock for the synthesis of other chemicals [3].

For this purpose, it is essential to develop novel, efficient and adaptable processes for CO_2 methanation. Nowadays, existing methanation processes are not optimized in term of catalyst, with respect to its activity and shaping. A global study to develop a methanation process of CO_2 is going to be accomplished in our project, starting by the assembly of methanation installation, passing by catalyst, kinetics and mechanistic studies, reactor and full process modeling to present finally a methanation process feasible at an industry scale.

In this work, a novel Ni-Co supported alumina catalyst was prepared by wet impregnation. The addition of cobalt to nickel alumina catalyst as promoter improves nickel dispersion and the resistance of the catalyst against coke deposition. The catalysts have the form of cylinders with 2 mm of diameter and 5 mm of length, to be directly used in a fixed bed industrial reactor. First, the alumina extrudates were prepared from alumina powder. Then, a series of nickel alumina catalysts with different amounts of nickel and cobalt between 5 %

and 25 % were prepared by wet impregnation and characterized by several techniques such as XRD, TPR, SEM, N_2 adsorption, and CO adsorption.

Those catalysts were tested in the methanation reaction in a tubular fixed bed reactor and an optimum amount of nickel was determined. The choice was based on the activity of the catalyst, methane yield and the dispersion of nickel on alumina. Then, bimetallic Ni-Co catalysts with different amounts of cobalt were prepared, characterized and tested in the same way to determine the optimum of cobalt. The full characterization by XRD, N_2 adsorption, CO and pyridine adsorption and TPR characterization of these catalysts helped us in explaining the observed catalytic results in terms of rates, conversions and selectivity. Figure 1 and 2 show the conversion of CO_2 and the selectivity in methane respectively.

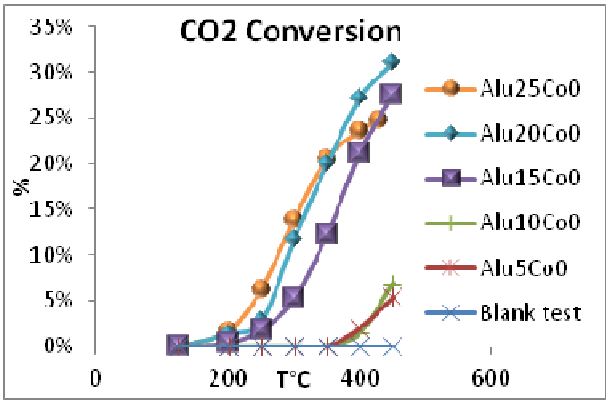

Figure 1. Effect of nickel content on CO_2 conversion

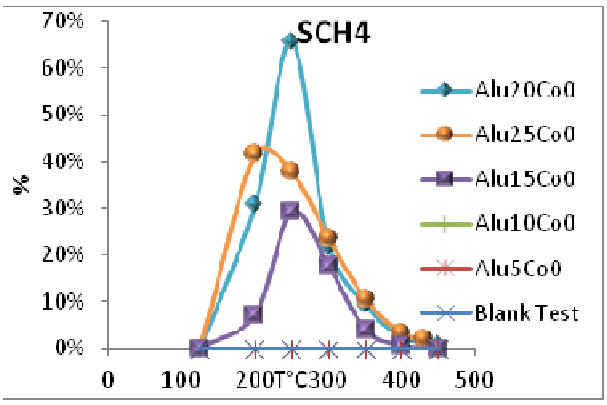

Figure 2. Effect of nickel content on methane selectivity

The kinetics of the methanation reaction over this novel Ni-Co optimized catalyst was experimentally studied in a fixed bed reactor by varying the experimental conditions such as flowrate, temperature, and reactant concentration. External and internal limitations were theoretically studied to be incorporated in the kinetic model. Finally, a heterogeneous kinetic model of Langmuir type was proposed where intermediate species such as CO or adsorbed dissociated molecules are taken into account. These species have been identified by in situ-operando technique.

Conclusions

Ni-Co/γ-Al_2O_3 catalyst with optimum amounts of nickel and cobalt toward methanation was prepared and characterized by several techniques. It was tested for CO_2 methanation under partial vacuum. Experimental results show that CO_2 conversion and CH_4 selectivity are affected by metal content. The addition of cobalt helps to improve nickel dispersion and helps in the catalyst resistance against coking. The kinetic study leads to a heterogeneous model of Langmuir type, which permits a better understanding and scale up of the methanation industrial process.

References

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Keywords
Methanation , Ni-Co/γ-Al_2O_3 catalyst, kinetics, methane