

SYNTHETIC NATURAL GAS PRODUCTION THROUGH HIGH PRESSURE METHANATION OF CARBON DIOXIDE

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Abstract

Hydrogenation of carbon dioxide at high pressure (up to 30bar) was investigated in this work. A novel Nickel-Aluminum hydrotalcite catalyst has been prepared, tested and compared to a commercial catalyst under high-pressure conditions. Such a system allows to obtain sufficient conversion at relatively low temperature (300°C) and contact time (0.1-0.2 s) to produce a synthetic natural gas (SNG) with the adequate grade to be directly injected in the natural gas existing infrastructure. The reaction kinetics has been investigated in the range of low temperature and high pressure values, with particular care to the reverse “reforming” reaction close to equilibrium. Both power law rate equations and mechanistic LHHW-type expressions have been evaluated (with or without a water inhibition effect term) in order to describe the methanation kinetics.

Keywords

Synthetic natural gas, methanation, nickel catalysts, hydrotalcite.

Introduction

“Power-to-gas” represents an interesting way to chemically store large amounts of energy peaks, especially when produced from renewable sources. According to this pathway, surplus and low-priced electricity can be used to produce hydrogen via water/steam electrolysis (Giglio, 2015). Then, hydrogen can be converted into methane by reacting with carbon dioxide through a catalytic methanation reaction (known as Sabatier reaction). The so-produced gas (SNG – “synthetic natural gas”) could be directly injected in the natural gas distribution grid (i.e., an already existing infrastructure). Nickel-based catalysts represent the main and more studied system because Ni is cheaper than other transition metals (e.g., Rh and Ru); catalysts composed by nickel supported on several oxides have also been analyzed (Gao, 2015). Recently, research focused also on high-loaded Ni hydrotalcite catalysts due

to the high activity showed (Abelló, 2013). Nevertheless, few studies deal with high pressure methanation of CO₂ and its kinetics. In this work, the results of a methanation test campaign at high pressure are presented, with the aim of investigating the reaction kinetics over a novel catalyst under real applicative conditions.

Methodology

A test rig has been designed and set up in order to perform tests at high pressure (up to 30 bar). Catalysts screening carried out at atmospheric pressure and conventionally diluted reactants concentrations showed superior performance of hydrotalcites with respect to oxides-supported nickel catalysts. Hereafter, for the sake of brevity, only the results pertaining to two catalysts are

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discussed: a Nickel-Aluminum hydrotalcite (HT) and a commercial catalyst ($\text{Ni}/\gamma\text{-Al}_2\text{O}_3$) produced by British Gas (CRG-F). Ni-Al hydrotalcite (HT) catalyst was prepared by co-precipitation method, by using nitrates salts as precursors of Ni and Al, in alkaline solution. HT was synthesized as a powder, while CRG-F was available in pellets. Both catalysts have been tested as ‘small size’ particles (250-900 μm) for comparison purposes. Moreover, the pressurized methanation experiments were carried out on CRG-F pellets ($\approx 3000\ \mu\text{m}$) too. Hydrotalcite sample has been characterized through BET analysis, XRD, H_2 -TPR, CO-TPD, TG-DSC and HR-TEM.

The chosen methanation concept (see Figure 1) consists of two isothermal reactors operating at 300 °C and 15 bar with an inter-condensation (water removal favors methane formation from a thermodynamic standpoint). Such a configuration ensures low thermal stress in the first reactor.

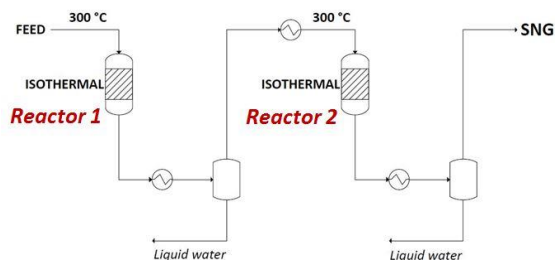


Figure 1. Methanation concept for SNG production

The main purpose of the experimental campaign was to simulate both the first and the second reactor and consequently modeling the corresponding kinetics. Thus, two different inlet mixtures have been involved: the first one (‘Reactor 1’) consists of hydrogen plus carbon dioxide stoichiometric feed ($\text{H}_2/\text{CO}_2=4$) diluted with nitrogen (10%vol.), while the second one (‘Reactor 2’) still presents a stoichiometric H_2 plus CO_2 with a high methane content (60%) and the same N_2 dilution (10%).

Results and discussion

The hydrotalcite sample presents a porous structure, typical of hydrotalcites. A surface area of $\approx 185\ \text{m}^2/\text{g}$ was measured for both calcined HT and CRG-F from BET equation. From TPR tests, it results that not all the NiO present in hydrotalcite sample undergoes reduction, which is the part encapsulated in spinel-like metastable structure. Figure 2 shows the comparison between hydrotalcite and CRG-F, for methanation tests at 15 bar. The performance of the two samples was very similar. In Figure 3 activity results with CRG-F pellets at 15 bar are presented. Also in this case the numbers 1 and 2 refer to the inlet mixtures.

Conversion with pellets is interesting for any industrial applications of the concept, but is obviously lower than the corresponding crushed powders, due to the higher pore diffusion resistance, as numerically evaluated and demonstrated. Nevertheless, using the maximum conversions experimentally obtained for the two inlet mixtures (93.2% for ‘Reactor 1’ and 82.8% for ‘Reactor

2’), the outlet synthetic gas presents low hydrogen (<5 vol.-%) and high methane content (>92.5 vol.-%). Thus, the obtained overall CO_2 conversion in the two reactors is 98.8%, and enables the production of SNG that could be directly injected in the natural gas distribution grid.

The experimental campaign at higher values of space velocity better discriminated the two catalysts’ activity, showing excellent performances of the hydrotalcite catalyst. Stability tests were also performed: hydrotalcite sample seems to show higher stability and very low activity degradation rate with respect to the commercial sample.

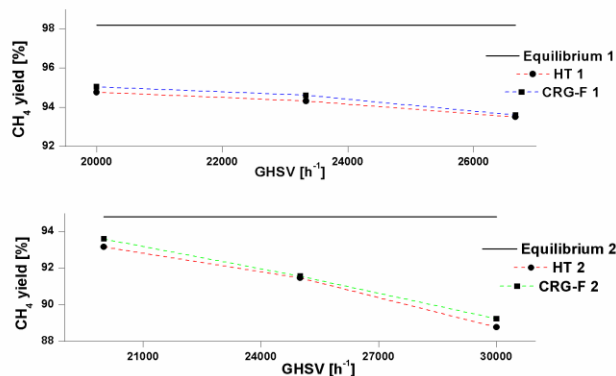


Figure 2. Results at 15 bar with hydrotalcite (HT) and commercial catalyst (CRG-F). ‘1’ and ‘2’ refer to ‘Reactor 1’ and ‘Reactor 2’ inlet mixture, respectively.

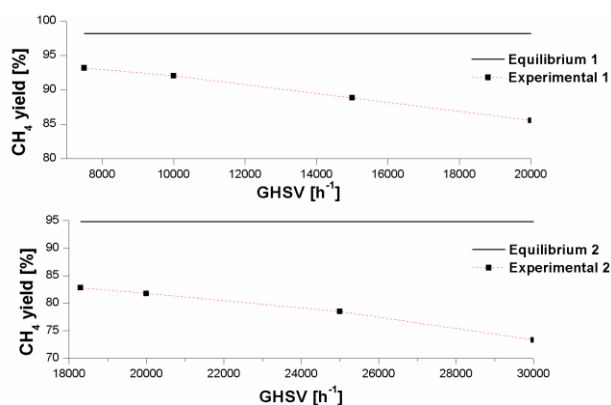


Figure 3. Results with CRG-F pellets at 15 bar.

Acknowledgements

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