

ENERGYPOLIS SEMINAR

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Water gas shift catalysts for pure hydrogen production from biomass steam gasification

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Gas production in the optic of biomass gasification at atmospheric pressure is well known [1]. Hydrogen in the obtained gaseous mixture can be increase by the water gas shift reaction (WGS), before using it for energy source. The novel utilization of alumina ceramic foams (figure 1) in place of supports for the WGS catalyst leads to good efficiency of the catalysts, even at atmospheric pressure, and allows decreasing the pressure drop in the system. It is necessary to proceed to a washcoat deposition, chosen to be Cerium oxide, before the catalyst's deposition. It leads to an increase in the specific surface area and a better dispersion of the catalytic phase. Iron is typically used for High temperature WGS (300-500 °C), and copper for low temperature WGS (150-300 °C). Another advantage of CeO₂ is the oxygen storage, which can limit coke formation during the reaction [2].

Cerium deposition and iron deposition are performed in two steps by dipping the foam in an aqueous cerium nitrate or iron nitrate solution. After drying, the foam is calcined for 4 h at 400 °C or 450 °C. Characterizations are performed by different methods (optical microscopy, X-Ray diffraction, BET analysis, Temperature programmed reduction). Pressure drop measurements are performed at 25 °C under 450 ml/min of air before catalytic tests.

The active phase in high temperature WGS reaction is the magnetite (Fe₃O₄). It is not necessary to reduce the catalyst before the reactivity test. The catalyst is reduced in-situ, in presence of the gas mixture corresponding to the gas mixture observed at the gasifier outlet (H₂, CO, CO₂, H₂O, N₂, CH₄). Different parameters were studied: the H₂O/CO ratio (0.65 to 3), the residence time (RT = 0.38 to 1.5 seconds), the temperature (300 to 600 °C), the composition of catalysts (different amounts of iron oxide and cerium oxide) and the porosity of the foam (30 ppi or 45 ppi). By adjusting the conditions to H₂O/CO=2, T=550°C, RT=0.38s, 5.8wt.%Fe/4.4wt.%CeO₂/45ppi, we obtain a CO conversion of 40%.

The active phase in low temperature WGS reaction is metallic copper (Cu⁰). A pre-reduction (300 °C for 1h, under 50 ml/min 40%H₂ in N₂) is necessary; it leads to a better activation of the catalyst, and higher CO conversions. The low temperature catalysts were used with the same gas mixture that for high temperature catalysts. Different parameters were studied: the influence of the pre-reduction, the temperature (150 to 300 °C), the composition of the catalysts (different amounts of copper and cerium oxide), and the porosity of the foam (30 or 45 ppi). By adjusting the conditions to H₂O/CO=2, T=300°C, pre-reduction, RT=0.38s, 5.4wt.%Cu/9.3wt.%CeO₂/45ppi, we obtain a CO conversion of 43%.

After tests characterizations were performed by X-Ray diffraction. We can see the presence of the active phase for the high temperature catalyst and for the low temperature catalyst.

Particles size calculations shows only a little increase in iron oxide and cerium oxide particles size. In the case of the low temperature catalyst, we do not see any increase in copper or cerium oxide particles size, even after re-using the catalyst for several reactivity tests.

Iron-based (HT) and copper-based (LT) catalysts were finally used in combination, in order to obtain an optimised CO conversion.

A kinetic study was performed for each catalyst. The adjustment of different kinetic parameters leads to adapted kinetic models based on the mechanism of the reaction on each catalyst [3-4].

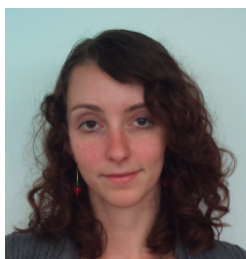
References:

[1] K. Maniatis ; Progress in biomass gasification: an overview. General Directorate of Energy & Transport, European Commission in Progress in A.Bridgwater (ed.) Thermochemical Biomass Conversion, pp. 1-31 Blackwell Sciences Ltd Oxford (2001).

[2] R. Di Monte, J. Kašpar ; *Catalysis Today*, 2005, **100**, 27-35.

[3] M. I. Temkin, *The Kinetics of Some Industrial Heterogeneous Catalytic Reactions*, Academic P. New York,

[4] N. E. Amadeo and M. a Laborde, "Hydrogen Production From the Low-Temperature Shift Reaction : Kinetics and Simulation of the Industrial Reactor Cp," *Int. J. Hydrog. Energy*, **1995**, vol. 20, 949.



CV: Dr. Charlotte Lang

Born in 1988 in Strasbourg, France, Charlotte Lang obtained her master graduation in 2012 from the University of Strasbourg. During the end-cycle internship, she worked at ICPEES on olivine-based catalyst for the steam reforming of toluene. She finally pursue her studies with her thesis at ICPEES to obtain her PhD degree in April 2016. Her doctoral thesis was integrated to the European project UNIfHY. She worked on the development of water-gas shift catalysts to produce pure hydrogen from biomass steam gasification.