

## Does the Fischer Tropsch reaction occur on the same catalytic site as the water gas shift reaction?

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### Introduction

The question whether the FT and the WGS reaction occur on the same catalytic site is a controversial topic<sup>1</sup>. Most reports propose that FT and WGS proceed on different sites, with carbide sites responsible for FT synthesis and Fe<sub>3</sub>O<sub>4</sub> as the active phase for the WGS reaction<sup>2</sup>. Experimental results were obtained in a lab scale CSTR (continuously stirred tank reactor) using a doubly promoted (Cu and K) precipitated Fe catalyst

### Materials and Methods

TCD GC analysis on the fresh feed and tail gas leaving the reactor was used with an internal standard to calculate Fischer Tropsch and Water Gas Shift reaction rates. Online GC analyses were done every 20 minutes to enable the calculation of rates on a continuous basis. Sufficient time (residence time distributions experiments were done for the reactor system) was also allowed for the system to reach equilibrium after changes were made to the reactor system before analyses were done on the tail gas.

### Results and Discussion

Reactions done under different space velocities showed that an increase in the space velocity gives a decrease in water gas shift reaction rate (corresponds to a decrease in water partial pressure in the reactor). A decrease in space velocity also gave an increase in the water gas shift reaction rate and corresponds to an increase in water partial pressure in the reactor). These results strongly suggest that water is a reagent for the water gas shift reaction and not necessarily the surface bound hydroxyl groups. Reactions done with the co-feeding of water also show an increase in water gas shift activity and support these findings. Careful interpretation of these results led us to conclude that after dissociation of CO with the formation of surface bound oxygen/hydroxyl groups, these oxygen species react with hydrogen and form water that leave the catalyst surface. This will explain the influence of changing the space velocity and co-feeding water on the water gas shift reaction rate. This means that water has to re-adsorb onto the surface and dissociate into hydroxyl and hydrogen species that react further to form CO<sub>2</sub> and Hydrogen. If FT and WGS occur on the same catalytic site then the WGS reaction rate will not be very sensitive to any change in the water partial pressure in the reactor and will show good correlation with the FT rate (the product of the FT reaction is a reagent for the WGS reaction and since they occur on the same site the two reaction rates should be closely correlated). Another argument based on solubility's can also be used to show that the water that needs to re-adsorb will be more reactive towards a more polar catalyst

surface than the predominantly non-polar FT active site. These arguments will be used to show that WGS and FT reactions not only occur on two different sites but that the hydroxyl species formed after CO dissociation is converted to water that leave the catalyst surface and re-adsorb to react further and produce CO<sub>2</sub> and hydrogen.

### Significance

The significance of these findings is that the WGS and FT rates could be, to some extent, independently varied (since they occur on two different sites) to allow the design of a process with the optimum usage ratio (Hydrogen consumed/CO consumed) and allow efficient recycle of the reactant gas.

### References

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