

Reactive Carbon as an Intermediate for the Industrial Production of Hydrogen or Methane

by

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Introduction

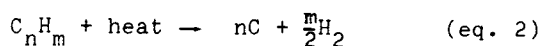
It has been known for a long time that reactive carbon can be deposited from carbonaceous feed ¹⁻³. In recent years researchers were able to produce fibrilous carbon even in macroscopic proportions ⁴⁻⁵.

Our goal was to demonstrate the feasibility of using reactive carbon as an intermediate for the industrial production of hydrogen or methane. By using this process, low BTU feed gases can be upgraded to high purity hydrogen or methane through the catalytic formation of surface carbon.

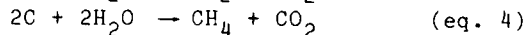
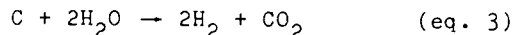
The first step involves the deposition of carbon by the disproportionation of CO (Boudouard reaction):



or by the catalytic pyrolysis of hydrocarbons:



The deposited carbon then can be removed by steam to form hydrogen or methane:



Suitable candidates, as feedstocks for our scheme, include gases from air gasification of coal, shale oil retort off-gas, or gas from the Exxon Flexicoker® process.

Experimental

The catalytic reactions were carried out in a small fluid bed constructed of a 1" I.D., approximately 32" long quartz tube fitted with a porous quartz disk to hold the catalyst. The advantages of using a quartz reactor instead of one made out of steel were that one could observe the catalyst during the reaction and, more importantly, the walls of the reactor were inert, therefore no carbon deposition took place on the surface of the reactor.

Heat was provided by a Lindberg Type 54032 split tube furnace. The temperature was at 450°C during carbon deposition and at 550°C during carbon removal. The reactions were carried out at atmospheric pressure.

The progress of the reactions were monitored by measuring the tailgas flow and analyzing the product gases periodically using a Carle 311 H gas chromatograph.

Results and Discussion

There are two main obstacles to using carbon as an intermediate for an industrial process to produce hydrogen and methane. One is the physical deterioration of the catalyst; the other is the reduction in chemical reactivity.

Baker (Exxon), and others reported on the tremendous destructive force exhibited by the deposited carbon. Conventional catalysts breakup by the carbon growth. Union Carbide circumvents this problem in the COthane process by depositing only a very small amount of carbon. We wanted to design a catalyst which could handle a commercial quantity of carbon, yet remains physically stable. We found that the catalyst retained its physical stability when the carbon was deposited in the pores of the catalyst.

In the experiments carbon was deposited to various concentration levels in order to study the effect of carbon level on the catalyst stability and the chemical reactivity of the carbon. Then the deposited carbon was removed by steam and the catalyst was examined by scanning electron microscope (SEM). The results of the SEM were surprising. No significant breakup of the catalyst particles was observable up to 40% carbon loading. We found that the size of the catalyst particles increased after carbon was deposited into the pores. This indicates that the particles remained intact by stretching.

The various carbon loading levels and the corresponding carbon deposition rates observed are shown in Table 1.

C LOADING		C DEPOSITION RATE (gC/hr/g Metal)
FROM (%)	TO (%)	
0	9.8	0.62
0	19.0	0.64
0	20.5	0.69
0	22.2	0.58
0	30.3	0.72
0	40.4	0.74

The above rates are fairly constant, independent of carbon levels, and show no sign of declining reactivity.

The carbon removal rates were also constant and independent of the carbon levels until the remaining carbon reached <10% carbon loading. A typical steaming rate curve is shown in Figure 1.

Two types of carbon deposits were found, amorphous and filamentous. Both types of carbon exhibited similar reactivity. No significant amount of unreactive carbon ("dead carbon") was detected.

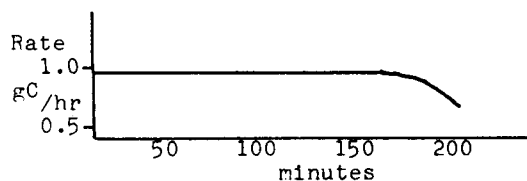


Fig. 1. Typical steaming rate curve.

Conclusion

From the data accumulated during these experiments we have concluded that our catalyst can tolerate carbon loading up to at least 40% level without exhibiting physical breakage. The main reason for this physical toughness appears to be the stretching of the catalyst particles. We have also concluded that reactive carbon can be used as an intermediate for the industrial production of hydrogen or methane.

Acknowledgement

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