PURE HYDROGEN PRODUCTION FROM SYNGAS BY STEAM-IRON PROCESS USING NANOPARTICLE IRON CATALYST

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Introduction

Stem-Iron process has been used in the early 1900s for the commercial production of H_2 at relatively higher temperatures in the range between 750 and 850°C.[1] Such high operating temperatures are necessitated because of the use of cheap, low reactivity iron oxide ores. However, these processes have been later abandoned due to severe degradation of the iron oxide ores within a few cycles.[2] Recently, interest in the steam iron process has been revived due to its ability to produce pure H_2 for fuel cell applications.[3] RTI has been developing a novel moderate temperature (400–550°C) steam-iron dual-reactor fluidized-bed process for producing pure H_2 byproduct from coal gasification-derived hot syngas in an integrated gasification combined cycle (IGCC) power plant. Development of an attrition-resistant and highly reactive iron oxide "catalyst" is the key to the commercial success of the process. To achieve these properties, supported nanoparticle iron oxide materials are synthesized using methods typically used for preparing supported catalysts.

Thermodynamic Analysis

The inlet iron oxide for the steam iron process is hematite (Fe_2O_3) that easily gets reduced to magnetite (Fe_3O_4) in the presence of syngas, a mixture of mainly CO, H_2, CO_2 and H_2O. Thermodynamic analysis using a typical syngas showed that the magnetite can be further reduced to either wustite (FeO) or metallic iron (Fe) depending on operating temperature. Re-oxidation to Fe_2O_3 was thermodynamically highly unfavorable using H_2O, thus the process cycle needed to operate between Fe_3O_4 and either FeO or Fe. High operating temperatures (750-850°C) favored reduction to FeO using both H_2 and CO whereas temperatures below 550°C favored reduction to Fe using only CO. Based on this analysis, the proposed novel process consists of the following redox cycle as shown in equation 1 and 2:

Reduction: $Fe_3O_4 + 4CO$? $3Fe + 4CO_2$ (1)

Oxidation : $3Fe + 4H_2O$? $Fe_3O_4 + 4H_2$ (2)

Materials and Methods

A series of iron oxide catalysts containing 20-40 wt% Fe_2O_3 supported on Al_2O_3, SiO_2, zeolites, and activated carbon were synthesized by homogeneous alkalinization method.[4] The redox properties of these catalysts were determined by H_2-TPR.[5] Their performance in the steam-iron process was evaluated in a thermo-gravimetric analyzer (TGA) by monitoring the weight changes during reduction using a simulated syngas (molar composition provided in **Figure 1**) and weight gain during oxidation using 29 volume % steam in an inert gas.

Results and Discussion

As can be seen from the TGA results of a two cycle test (**Figure 1**), iron oxide reduction occurs in two steps, a fast step for the reduction (Fe_2O_3? Fe_3O_4? Fe) of reactive iron oxide particles and then a slow step presumably of less reactive particles. For a short contact time fluidized-bed reactor, only the fast reduction step is of importance. Steam oxidation of Fe? Fe_3O_4, as expected, proceeds at a slower rate compared to the first reduction step.

Among the catalysts screened in TGA, iron oxide supported on USY zeolite exhibited the best performance. H_2-TPR revealed that the iron oxide particles are homogeneously distributed on the USY zeolite compared to Al_2O_3 and SiO_2 supports. The data shown in **Table 1** indicate that the extent of reduction in the second cycle and the extent of oxidation increases with increasing iron oxide loading from 20 to 40 wt%. These catalysts are being modified with promoters to further improve the performance. Selected catalysts are also being evaluated in redox cycles using a fluidized-bed reactor.

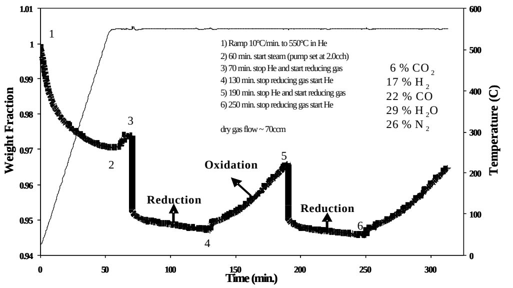

Figure 1 TGA profile for the two-cycle steam-iron process over $40\%Fe_2O_3/Al_2O_3$

Table 1 Two-cycle Steam-Iron Process TGA Results of Selected Catalysts at 550°C

Catalyst	Reduction Cycle-1 Fe_2O_3 to 2Fe	Oxidation Cycle-1 3Fe to Fe_3O_4	Reduction Cycle-2 Fe_3O_4 to 3Fe
	% Reduced	% Oxidized	% Reduced
20% Fe_2O_3/USY	41.3	11.8	13.2
30%Fe_2O_3/USY	28.8	13.9	18.8
40%Fe_2O_3/USY	35.8	16.3	21.5
40%Fe_2O_3/Al_2O_3	24.2	19.0	19.6

Significance

The moderate temperature steam-iron process integrates very well in an IGCC plant for co-production of hydrogen and electricity. Development of an attrition-resistant and reactive iron-oxide catalyst as described here can lead to commercial production of high purity and high pressure H_2 from domestically available resources such as coal and biomass.

References

1 Messerchmidt, *German Patent* DE 266863, Germany (1911)
2 Elliot, M.A., ed., "Chemistry of Coal Utilization," Second Supplementary Volume, Wiley Interscience Publication, pp 1686-1688 (1981).
3 Takenaka, S., Nomura, K., Hanaizumi, N., Otsuka, K. *Appl.Catal.A.* 282, 333 (2005).
4. Velu, S., Gangwal, S.K., and Nelson, T.O. Highly dispersed nickel hydrogenation catalysts and methods for making the same. *U.S. Patent application No*. 60/849,479 (2006).
5 Velu, S., and Gangwal, S.K. *Solid State Ionics*, 177, 803, (2006).