CATALYSIS AND OPPORTUNITIES FOR THE PRODUCTION OF H_2

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ABSTRACT

This presentation will describe the increasing importance of H_2 in our world. Since the bulk of the world's H_2 is produced by catalytic processes, often involving multiple types of catalysts, it is clear that catalysis plays a critical role in the production of H_2. The focus will be on the use of catalysis in the current and future production of H_2. Steam methane reforming will be a focal point of the discussion, and it is interesting to view the large number of catalysis steps that are used in this major technology. Some background will be provided to give a perspective of the dramatic change in the supply and demand for H_2 in the past decade, followed by a review of how it is produced commercially, with a view to how multiple types of catalysis contributes to the total process for H_2 production. Issues of carbon management and CO_2 emissions will also be discussed. In addition, some alternative catalytic approaches [fuel cells, photocatalysis, membrane reactors, etc] for H_2 production will be discussed and specific barriers to progress and opportunities for further research in this area.

INTRODUCTION

Hydrogen is forecast to become a major source of energy in the future. Prior to the early 1990s, H_2 was plentiful with refineries being major producers. Now that picture has changed due to environmental demands to reduce sulfur emissions and the production of less aromatics for gasoline; thus, refineries have had to build additional H_2 production units nearby [1]. H_2 offers the potential of a clean burning fuel if it is combined with only O_2 and would result in no extra CO_2 emissions, as long as H_2 were obtained from non-fossil fuels . With H_2 production being localized and without a large scale distribution system to move this hydrogen to more customers, H_2 is currently not a cheap fuel alternative; it simply has too much value as a chemical reductant. Limitations of space for this manuscript do not permit a complete discussion below of issues associated with the production of H_2; thus, the reader is encouraged to examine the references for greater detail.

Steam methane reforming, SMR, is the largest and generally the most economical means to produce H_2. SMR is not just one reaction, but a series of well balanced operations often including most of the following: desulfurization, pre-reforming, reforming, high and low temperature water gas shift, methanation, and NOx removal. The key reaction is represented by equation 1. Several good reviews describe this and other commercial approaches to the

$$CH_4 + H_2O \rightarrow CO + 3\,H_2 \qquad (1)$$

production of H_2 [2,3]. Since the desired product is H_2 and not CO, the CO is usually taken through the water gas shift reaction to produce more H_2 (equation 2). This produces CO_2; in

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (2)$$

Table 1
Steps in SMR which employ catalysts [from reference 1]

Process operation	Temperature, °C
Sulfur conversion [HDS]	290-370
H_2S removal [ZnO]	340-390
Chloride removal [Al_2O_3]	25-400
Pre-reforming	300-525
Steam methane reforming	850
High temperature water gas shift	340-360
Low temperature water gas shift	200
Methanation	320
NOx removal [NH_3 SCR]	350

addition, one must consider that the heat derived to drive the very endothermic reaction'1, often comes from natural gas burners, which also produce more CO_2. There is an aggressive worldwide R&D effort to develop other cost effective and energy efficient means to produce H_2, especially for small volume use in remote areas of the world.

H_2 production is linked to CO_2 production when fossil fuels are reformed. In order to reduce CO_2 emissions, use of natural gas instead of coal [a higher C/H feedstock] is preferred if one must use a fossil fuel. Fuel cells as a source of power usually consume H_2. While fuel cells are widely promoted for their fuel efficiency, they must be assessed based upon the levels of CO_2 produced from the fuels used to power the fuel cell. In the near term, there is interest in using increased carbon sequestration to provide some intelligent carbon management approaches for fossil fuel routes to H_2. In the long term, we need to focus on the production of H_2 from non-fossil fuel sources or on truly renewable fuels.

There has been much excitement in the literature to use CO_2 as a feedstock to make chemicals. However, even if we had existing technology to covert CO_2 to more valued chemicals, the volume of chemicals would still be very small relative to the level of CO_2 emissions being discussed. Further, using H_2 on a massive scale to chemically reduce CO_2 to CO or CH_4 has questionable value because of the cost of the H_2. In addition, most of the world's H_2 is made from SMR which co-produces CO_2; thus it makes little sense to use SMR derived H_2 to reduce global CO_2 levels.

BARRIERS TO PROGRESS

In considering new approaches to H_2 production and/or SMR improvements, several technical barriers exist:

- Heat transfer seriously restricts operating temperatures
- More literature data needs to be gathered by studying reactions closer to the high pressure operations of existing processes and the demands for high pressure H_2
- Advances in reactor design are needed
- Overcoming limitations of material components with regard to metal dusting or high temperature seals
- Need for more ex-situ surface science techniques which allows one to characterize working catalysts under extreme temperatures [850°C] and pressures [400 psig]
- Developing process conditions which assure safe operation

OPPORTUNITIES FOR ADDITIONAL RESEARCH

Overcoming the barriers noted above will also open up new avenues for research, including:

- More laboratory units capable of studying SMR under actual process conditions
- Need for a simple, accelerated aging test to assess catalyst life
- More efficient ways to provide or utilize the energy needs for SMR
- Catalysts which minimize the formation of elemental carbon
- Non-fossil fuel sources for commercial H_2 production
- Use of CH_4 as a substitute for H_2 in the production of chemicals

ALTERNATIVE MEANS FOR PRODUCING H_2

Identifying the barriers, enables one to define new opportunities for research, not only for existing approaches but also for alternative means to produce H_2. While there is a need and demand for new routes to cost effective production of large volumes of high pressure H_2, there are niche opportunities where small volumes of low pressure, very pure H_2 are also attractive. Technologies which could address these needs [with some specific hurdles in brackets] include:

- methane decomposition [need to resolve how to handle and use all the huge amount of by-product carbon]
- use of membrane reactors [still limited by materials deficiencies, high temperature seals, and membrane configuration issues] [5]
- solar energy for electrolysis of water [must use visible light with high quantum yields]
- selective oxidation of methane [must provide convincing evidence for safe operation]
- oxidative dehydrogenation [issues of by-product coke formation which leads to fouling and an olefin co-product which must be in huge demand]

- biomass conversion [need pilot demonstration which addresses all the scale up, cost, and environmental issues]

SUMMARY

Steam methane reforming is the dominant technology for H_2 plants, and it comprises many different catalytic operations, including desulfurization, pre-reforming, reforming, high and low temperature water gas shift, methanation, and deNOx. As long as natural gas and petroleum based hydrocarbons are still relatively low cost fuels, SMR will continue to be a cost effective approach for making H_2. Steam reforming is a mature technology, but there is fertile ground and room for technological improvement. Beyond 2010 future economic or environmental issues may eventually force adoption of substitute, alternative technologies since steam reforming is an energy intensive, endoergic process, CO_2 is a co-product, and H_2 purification is necessary. At the fundamental research level, there is a need for more catalyst studies at >20 atm where the chemistry is actually practiced and the bulk of customer demand exists. The life of the catalyst is an important criteria in benchmarking new catalysts versus commercial SMR catalysts and suitable accelerated aging tests need to be devised which provide meaningful assessments of alternative catalysts or technologies.

There are a number of emerging and attractive approaches to H_2 production, but the greatest opportunities in the future would seem to lie with non-fossil fuel based H_2 technologies, where major breakthroughs are needed. In considering new technologies for H_2 production, one has to consider the entire process. That is, one must have separation and purification steps, consider net energy demands and balance, the quality of the feed, etc. Ultimately, the route one chooses to produce H_2 will be a function of not only the technology advances, but also economics, the environment, specific customer needs, and market demands.

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