Novel Catalyst Development and Process Optimization for CO₂ Reforming of CH₄

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The grant from DoE/EPSCOR covered funding for the period 3/1/99 – 3/1/02. The present Final Report describes the main findings obtained by the two research groups, who worked together in the study of novel catalytic materials and optimal process conditions for the conversion of CH₄ with CO₂.

A) Development of novel catalyst for the CO₂ Reforming of CH₄

The CO₂ reforming of CH₄ is been intensively investigated for the production of synthesis gas as a complementary process of the well-established steam reforming. The possibility of utilizing CH₄ and CO₂ when they are simultaneously present in natural gas reservoirs as well as the H₂/CO product ratio, which is lower than that of steam reforming, make this process attractive for some applications. The primary difficulty associated with the applicability of the CO₂ reforming process is finding a suitable catalyst that will not deactivate under the deactivating conditions needed for this reaction. Since the reforming reaction is highly endothermic, high operating temperatures (~1073 K) are required to obtain significant conversions. At such high temperatures and in the presence of high concentrations of carbon-containing compounds, the catalyst is susceptible to deactivation, primarily by carbon deposition.

The deposition of carbon in this reaction strongly depends on the type of metal being used. Although, in many reactions Group VIII metals are less prone to coking than Ni, Co, and Fe, their ability to operate with low carbon deposition under CO₂ reforming of methane is strongly related to their activity for CO₂ dissociation. For example, Ru and Rh are very active for CO₂ dissociation and they have been found able to effect the CO₂ reforming of CH₄ in the range 873-1173 K without carbon deposition. Although the type of support used has been shown to have an effect on the methane reforming activity of metals like Ru or Rh, which are efficient for dissociating CO₂, those effects are much less crucial than in the case of Pt and Pd. This difference is due to the different abilities of the metals for CO₂ dissociation. A metal able to dissociate CO₂ is very efficient in eliminating the carbon produced by the methane decomposition. By contrast, Pt or Pd require the assistance of the support to keep their surface free of carbon. Seshan et al. [1, 2] first reported that ZrO₂ is a support that promotes stability of Pt, even under severe conditions. Our own investigations, with isotopically labeled molecules, showed that the ZrO₂ support has a strong effect on the activity and stability of the catalyst [3]. In those studies, we found that when the Pt/ZrO₂ catalyst was exposed to pulses of ¹³CH₄, formation of ¹³CO, together with small amounts of ¹³CO₂, was observed. X-ray absorption studies demonstrated that the metal particles were in the metallic state. Therefore, the only possible source of oxygen in this experiment was the support. It was then suggested that some of the carbon produced from the decomposition of ¹³CH₄ partially reduced the oxide support near the perimeter of the particle. This was a rather unexpected result, since zirconia is generally considered an unreducible support. However, in agreement with our results other authors have previously reported that a partial reduction of zirconia is possible at high temperatures [4]. The remaining ¹³C produced from the decomposition of ¹³CH₄ was deposited on the Pt metal. Subsequent pulses of ¹²CO₂ resulted in the production of both ¹²CO and ¹³CO, which supported the idea that carbon was removed from the metal particles under reaction conditions. The

results also showed that Pt is needed to catalyze the dissociation of CO₂ since ZrO₂ alone was not able to do it. Consequently, it was concluded that the dissociation either takes place near the metal-support interface, or it occurs on oxygen vacancies generated during the previous reduction of the support by the methane pulses, which in turn is activated by the metal.

More recently, we have reported that the use of promoters such as cerium oxide improves the activity and stability of Pt/ZrO₂ catalysts under severely deactivating reaction conditions [5-7]. We have interpreted the promoting effects of Ce in terms of a mechanism for the CO₂ reforming on Pt/ZrO₂ catalysts involving two independent paths [3, 5]. One of them is the decomposition of methane that occurs on the metal, resulting in the formation of hydrogen and carbon, and the other is the reaction of this carbon with oxygen to produce CO. This oxygen can either come from the ZrO₂ support near the metal particle, or from the decomposition of CO₂. In this dual path mechanism, the role of the support is very important. It participates in the dissociative adsorption of CO₂ near the metal particles, transferring oxygen to the coked metal and greatly accelerating the removal of carbon from the metal. Similar results were obtained on Rh/ZrO₂ by Efstathiou et al. [8], who demonstrated that the oxygen vacancies in the zirconia support could be replenished by oxygen from the dissociation of CO₂.

Cerium oxide is known to have a very high oxygen exchange capacity. This capacity is related to the ability of cerium to reversibly change oxidation states between Ce⁴⁺ and Ce³⁺ by taking or giving up oxygen. It has been shown [9, 10] that the reduction of Ce is not due to a direct release of O₂ to the gas phase, but through a surface reaction with a reductant such as CO, hydrogen, or a hydrocarbon. This reaction is believed to occur at the metal-support interfacial perimeter. Accordingly, the reductant adsorbed on the metal particle would get oxidized at the interface by oxygen from the support. Therefore, it is not surprising that the addition of cerium improves the activity of CO₂ reforming catalysts. A second important effect of promoters is the inhibition of Pt particle growth. This effect is not only beneficial for increasing the active metal surface exposed for reaction, but also for maintaining a high metal-support interfacial area, which is crucial for efficient cleaning of the metal particle.

During the last year, we have investigated the relationship between the reducibility of the support and the catalytic activity of supported Pt on a series of catalysts supported on ceria-zirconia mixed oxides. The supports were prepared by co-precipitation with varying Ce/Zr ratios. X-ray diffraction analysis indicated that, depending on the Ce/Zr ratio, solid solutions of cubic Ce_xZr_{1-x}O₂ can be formed. The reducibility of the supports was determined by XPS. After reduction at 773 K in hydrogen the fraction of reduced cerium (i.e., Ce³⁺) was found to vary with the Ce content, exhibiting a maximum at a composition Ce_{0.5}Zr_{0.5}O₂.

A good correlation was found between the reducibility and the catalytic activity. It was found that the conversion of methane and CO₂ obtained on the different catalysts after 22 h on stream went through a maximum as a function of Ce content in the support and that maximum occurred at the composition that exhibited the maximum reducibility. The

H₂/CO product ratio was also a function of the support composition, also presenting a maximum for the Pt/Ce_{0.5}Zr_{0.5}O₂ catalyst.

The amount and nature of carbonaceous deposits were investigated by combining temperature programmed (TPO) studies with X-ray photoelectron spectroscopy (XPS). The TPO profiles of all the spent samples revealed two oxidation peaks, one in the low-temperature region, 623 K – 723 K, and the other in the high-temperature region, 873 K - 973 K. The peak in the high-temperature region is dominant in the unpromoted catalysts, while the peak at low temperature is more prominent in the Pt/Ce_xZr_{1-x}O₂ catalysts. XPS exhibits three types of carbon with different binding energies on the spent catalysts, two of them are two forms of coke, and the third one is due to carbonates. However, all of the peaks decreased after an oxidation at intermediate temperatures (i.e. 723 K). Therefore, it appears that the different peaks observed in TPO are not due to different forms of carbon, but rather to different locations on the catalyst surface. The amount of carbonates on the spent catalysts increased with the Ce content, but the correlation between carbonate concentration and activity was not as good as that between reducibility of the support and activity.

Publications from the current project funded by DoE

- “Metal-support interactions on Pt/ZrO₂ catalysts for the CO₂ reforming of CH₄” S. M. Stagg-Williams, and D. E. Resasco. *Stud. Surf. Sci. Catal.* **130** (2000) 3663
- “CO₂ Reforming of CH₄ over Pt/ZrO₂ Catalysts Promoted with La and Ce oxides, S. M Stagg-Williams, F. Noronha, G. Fendley, and D. E. Resasco, *J. Catal.* **194** (2000) 240-249
- “Correlation Between Catalytic Activity and Support Reducibility in the CO₂ Reforming of Methane over Pt/Ce_xZr_{1-x}O₂ Catalysts”, Fabio B.Noronha¹, Eugene C. Fendley, Ricardo R. Soares, Walter E. Alvarez, and Daniel E. Resasco, , *Chemical Engineering Journal*, 82 (2001) 21-33

References

- 1 Seshan K., Ross J. R. H., Mercera P. D., and Xue E., German Patent DE 9400513 (1994)
- 2 Bitter J. H., Hally W., Seshan K., van Ommen J. G., and Lercher J. A., *Catal. Today* 29, 732 (1996)
- 3 Stagg, S.M., Romeo, E., Padro, C. and Resasco, D.E., *J. Catal.* 178, 139 (1998).
- 4 Tournayan L., Auroux A., Charcosset H., and Szymanski R., *Ads. Sci. Tech.* 2, 55 (1985)
- 5 Stagg, S.M. and Resasco, D.E., *Stud.Surf.Sci.Catal.* 119, 813 (1998)
- 6 Stagg-Williams, S. M., Soares, R., Romero, E., Alvarez, W. E, Resasco, D. E., *Stud. Surf. Sci. Catal*, 130, 3663 (2000)
- 7 S. M Stagg-Williams, F. B. Noronha, G. Fendley, and D. E. Resasco, *J. Catal.* 194, 240 (2000)

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- 8 Efstathiou A. M., Kladi A., Tsipouriari V. A., and Verykios X. E., *J. Catal.* 158, 64 (1996)
 - 9 Cordatos H., Bunluesin T., Stubenrauch J., Vohs J. N., and Gorte R. J., *J. Phys. Chem.* 100, 785 (1996)
 - 10 Putna E. S., Bunluesin T., Fang X. L., Gorte R. J., Vohs J. N., Lakis R. E, and Egami T., *Catalysis Today*, 50, 343 (1999)

B) Process Thermodynamic Analysis of CO₂ reforming of Methane

During this project a process thermodynamics analysis of the CO₂ reforming of methane aiming at the selection of optimal process conditions for the production of Syngas was studied. The results are summarized below. A draft of the paper that will be submitted for publication, which is a short version of a Master Thesis by Jose Fernando Cancino, is attached.

Two types of natural gases, one with almost no CO₂ and the other with a high content of CO₂ were chosen to investigate whether a single reactor or a combination of them can competitively produce Syngas. Addition of CO₂ and water to the inlet and intermediate streams is considered as means of adjusting conditions to reach the desired Syngas ratio.

Goals and Constraints

Specifically, the purpose of this study was to identify under which conditions (pressure, temperature, amount of water in the feedstock, and reactors scheme) the reforming of natural gas using steam and/or CO₂ is thermodynamically and economically optimal. The constraints are given by the following specifications:

- High methane conversion.
- The lowest possible CO₂ content in the product.
- The highest possible Syngas production rate.
- A low usage of steam is preferred

Thermodynamics

The key problem when dealing with CO₂ reforming of methane is carbon formation, which is favored at high temperatures and pressures. Therefore, it is desired to study the effect of pressure and temperature on the equilibrium, and once those conditions are set, it is desired to know how changes on feed composition affect the performance of a reactor scheme regarding Syngas yield, methane conversion, reactor duty, and CO₂ content in the outlet stream. It is assumed in this study that the reactor reaches equilibrium.

It is concluded that a process at atmospheric pressure is more convenient due to a higher methane conversion, Syngas yield, H₂/CO ratio, as well as reduced carbon formation when compared with a process at a higher pressure. On the other hand, the CO₂ content in the outlet stream is lower at lower pressure.

Handling so many variables at the same time motivates the search for a different type of diagram to represent a feedstock defined by the composition of CO₂, CH₄, and H₂O, which at the same time would give information on methane conversion, syngas yield, duty, and CO₂ content in the outlet stream. Rostrup-Nielsen¹ has suggested such a chart, which is expanded in this analysis to cover all the desired features. The equilibrium chart proposed was originally built to show how changes in feed composition affects the Syngas ratio produced, to predict savings on steam consumption, and to work on the safe side of the carbon

formation region. With the addition of constant methane conversion, Syngas yield, reactor duty, and CO₂ content at the outlet stream (Figures 1 and 2), the performance of a reactor scheme on the equilibrium chart can be represented.

Figure 1: Constant methane conversion and constant duty lines at 850°C and 1 atm.

Figure 2: Constant duty and CO₂ at the outlet stream at 850°C and 1 atm.

One of the most important economic indicators is the duty. To make a value of duty meaningful, the net amount of heat that needs to be supplied to the equilibrium reactor is calculated. It is assumed that most of the energy requirements for the reactor are recovered through steam generation and preheating of the feed. The duty is thus defined as the net amount of heat that needs to be supplied to the reactor after heat exchange of the feed with the outlet of the reactor. All the calculations performed to build these curves were done using Pro IITM (Simulation Sciences).

Single Reactor Configuration

The performance of a single reactor, series, and parallel reactors with both feedstocks has been analyzed on the equilibrium chart (Figure 3), as well as with the simulator to obtain optimum conditions that met the constraints set.

Figure 3: Single reactor with Terrell gas (left) and California gas (right), 1 atm and 850 °C

When processing Terrell gas, the use of CO₂ recycle does not have an advantage over the no-recycling option (more addition of water, more duty required, and a marginal increase in Syngas yield). On the other hand, when recycling CO₂ the separation and compression step and has to be considered. For California gas processing, the CO₂ recycling option does not help to obtain good Syngas yield or a high methane conversion, and the addition of CO₂ and water has to be considered to work far from the carbon formation region. In such case, recycling can be of value.

Series Reactors

The equilibrium chart is used to explore the operation of series reactors at a fixed temperature and pressure using both Terrell and California gas. Several arrangements of two series reactors were evaluated including addition/removal of CO₂ from the outlet stream from the first reactor and recycling CO₂. Figure 4 shows the series reactor scheme on the equilibrium chart for both Terrell and California gas. From this graph the optimal conditions for this reactor scheme can be obtained.

Figure 4: Series reactors with Terrell gas (left) and California gas (right), 1 atm and 850 °C

Parallel reactors

The next step is to evaluate the operation using a parallel arrangement of equilibrium reactors. One reactor works under steam reforming conditions and the other under CO₂ reforming conditions. Water is separated from the outlet streams, which are mixed to form the final outlet Syngas stream. CO₂ recycling after separation from the CO₂ reforming reactor has also been explored. The goal is to find the best set of operating conditions (maximum yield and methane conversion, while keeping at a minimum the amount of water added and the CO₂ flowrate at the outlet stream) under which CO₂ reforming of CH₄ is a good production scheme for several fixed H₂/CO ratios. Both extreme feedstocks are evaluated using this arrangement. Therefore, to accurately predict the behavior of parallel reactors a simulator is used with the following objective function, variables and constraints:

Objective function:	Minimize the duty (KJ/Kg-mol CH ₄)
Constraints:	H ₂ /CO syngas ratio = 2/1 Total X _{CH4} = 0.98, 0.99, 0.995, 0.9995 Gas flow (R _{x1} +R _{x2}) = 100 Kg-mol/hr (basis)
Variables:	Water to Reactor 1 (R _{x1}), Temperature of reactors, Flowrate of gas to reactors.

All these values are set in the optimizer and calculator to perform the calculations.

Conclusions

Optimal conditions of temperature and pressure as well as water addition and CO₂ recycling have been investigated

Assuming that a catalyst able to work under the predicted conditions exists (high temperature, presence of water, carbon deposition, etc.), the following conclusions are made:

Single reactor

- When using Terrell gas, recycling CO₂ increases the yield, the water required, the duty, and the methane conversion at constant desired H₂/CO ratios. The cost of CO₂ separation and recycling needs to be considered.
- For California gas processing, and working at low desired Syngas H₂/CO ratios, recycling CO₂ is not enough to get high yields and conversion. Thus, external CO₂ is needed.
- It is observed that the temperature required to get fixed methane conversion decreases as the recycle of CO₂ increases but the duty goes up. This effect plays a very important role in deciding to recycle CO₂. For example for the case with an H₂/CO ratio of 2/1, when recycling all the CO₂ the temperature can be reduced from 850°C to 767°C, allowing the catalyst to work under less severe conditions. The H₂O/CH₄ ratio also increases greatly. However, the duty of the reactor increases in approximately 5 % when going from 0% to 100% CO₂ recycle.

Series reactors

- When using Terrell gas the series reactors scheme has no advantage over the single reactor configuration because the duties obtained with series reactors are in all cases higher. When minimizing the duty, and, at the same time the usage of water in both reactors, the simulation gives a solution with lower steam consumption. However, the duty is still high in the order of 3.0 to 3.5 %.
- California gas is better suited for hydrogen processing through the Steam reforming process. For producing lower Syngas ratios, it needs CO₂ addition. Only when the cost of external CO₂ is zero or very low value, this alternative can be used effectively.

Parallel reactors

- This reactors scheme does not offer advantages over the single reactor scheme for both feedstocks processed because of the higher duty obtained at the same level of yield and conversion