

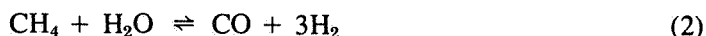
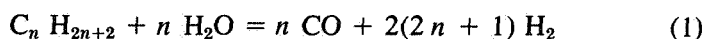
# Catalysts for Steam Reforming of Hydrocarbons

The major problem, carbon deposition, can be effectively minimized by adding potash to the catalyst system

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The formulation of a good reforming catalyst is complex because of the conflict between its important characteristics. In steam naphtha reforming, where carbon deposition is a very acute problem, the best solution is obtained with a catalyst system containing potash.

When hydrocarbons undergo steam reforming over nickel catalysts in the production of synthesis gas and hydrogen, the hydrocarbon may be considered to react with the steam to produce CO and H<sub>2</sub>, reaction 1, and then the methane-steam equilibrium 2 and the CO shift equilibrium 3 are set up:



These reactions take place simultaneously producing a mixture of H<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub> and excess H<sub>2</sub>O. The reforming reactions 1 and 2 are endothermic, so that the process is carried out in the familiar, heated tubular reformers at pressures up to 30 atm. and catalyst exit temperatures up to 900°C.

Nickel is the most effective catalytic metal. Reforming catalysts fall into two broad classes: "precipitated," in which nickel may be co-precipitated and mixed with other oxides such as Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, MgO, CaO and cement compounds; and "impregnated," in which a pre-formed support of alumina, MgO or spinel compounds are impregnated with a solution containing nickel and other compounds such as U<sub>3</sub>O<sub>8</sub>.

A reforming catalyst must be robust and have a high activity which is retained in service to ensure that the equilibrium gas composition is achieved. The catalyst containing nickel oxide and other compounds has to be reduced before use, and the formulation must be such that the reduction is rapid and complete to produce the maximum surface and the highest activity. At the same time, the catalyst must be selective and not form carbon by side reactions as it can partially obstruct the catalyst surface or block the reformer tube.

## Limits to the activity

The activity of a reforming catalyst depends on its nickel content, and with all catalysts reaches a maximum beyond which, however, activity can decrease. Table 1 shows the reforming activity of precipitated catalysts of differing nickel content.

The activity tests were carried out with pelleted catalysts in 1-in. diameter tubes. The catalysts were re-

**Table 1. Reforming activity and nickel content**

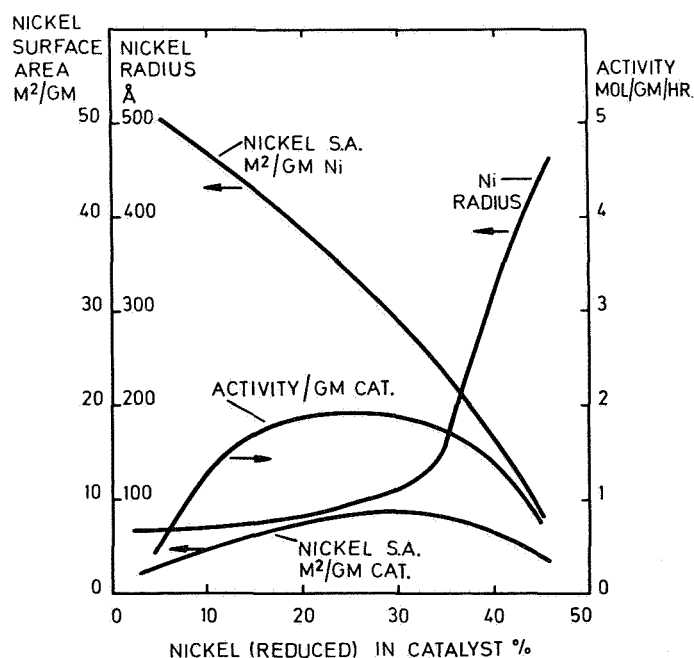
Catalyst No. 1		Catalyst No. 2	
Percent nickel	Percent CH <sub>4</sub> conversion	Percent nickel	Percent CH <sub>4</sub> conversion
10.6	10.3	19.3	15.5
13.9	13.4	21.0	18.2
17.9	19.8	22.1	20.4
20.8	20.1	23.8	19.6
25.8	20.6		

Notes: Feed, methane and steam. Steam/carbon ratio, 3.0 moles/atom. Pressure, 26 atm. Temperature, inlet 450°C, outlet 600°C. Space velocity (methane plus steam), 35,000 hr.<sup>-1</sup>

duced in 10% H<sub>2</sub> in steam for 24 hr. at 650°C, and were operated for 24 hr. at inlet temperature 450°C, exit temperature 750°C, to age them before test.

The results show that activity increases in proportion to the nickel content up to about 20%, but it is clear that above that concentration no increase in activity is obtained. A similar conclusion is derived from other work (1) with nickel-MgO catalysts the results of which are given in Figure 1.

In this case, there is little increase in activity with nick-



**Figure 1. Nickel content, surface area, size and activity.**

el contents higher than 15%, and activity actually decreases when the nickel exceeds 30%. The nickel surface area decreases with increasing nickel content; and above 30%, sintering is extensive, and the particle size increases rapidly giving rise to lower surface area and lower activity.

Such high nickel contents are not necessary in the impregnated type of catalyst, in which the metal is distributed along the surface of the pores of the support. On the surface, the nickel is more accessible and available for reaction than in the precipitated type of catalyst. The optimum metal concentration in an impregnated catalyst is therefore lower, being between 8 and 12% depending upon the support.

The activity of such an impregnated catalyst is comparable with that of precipitated catalysts of considerably higher nickel content. Thus in the activity test referred to earlier, in Table 1, an impregnated catalyst, 10% nickel on alumina, gave 20.9% conversion compared with 20.6% with the precipitated catalyst containing 25.8% nickel.

A catalyst is reduced in a reformer using a  $H_2$ -containing gas or natural gas, the temperature being 400-500°C at the inlet and 800°C at the exit. The inlet end of the catalyst bed is important because the reaction is initiated there and it can influence the performance of the whole reformer, for example, in regard to carbon formation as will be seen later. Reduction is slowest at the inlet and the time of reduction is influenced by the reducibility of the catalyst there.

Depending on the composition of the catalyst and its method of manufacture, the nickel oxide can form compounds, for example, of the spinel type such as nickel aluminate, which are difficult to reduce at temperatures below 600°C. Nickel oxide can also form solid solutions with MgO which are difficult to reduce; Takemura (2) showed that NiO reduced completely below 400°C while a 10% NiO-90% MgO solution reduced in two stages, the reduction being only 70% complete at 600°C. Nielsen (1) reports similar results with a series of catalysts based on MgO with different amounts of nickel; at the lowest nickel content (Ni/Mg 0.25) only 39% of the nickel was reduced by treatment in  $H_2$  at 850°C for 2 hr.

### Nickel sintering affects reduction process

Catalysts therefore differ considerably in the ease with which they can be reduced. The reduction process is complex because once it is started sintering of the nickel can take place. This is demonstrated in Figures 2 and 3, which show the nickel surface area obtained when two different catalysts were reduced with  $H_2$  at atmospheric pressure at different temperatures and for different times in the presence and absence of steam.

It is clear that the highest initial surface area is obtained when the reduction is done with pure  $H_2$ . It is a maximum at a temperature of about 600°C; at lower temperatures the reduction is not complete in the time of the experiment; at higher temperatures the area is lower

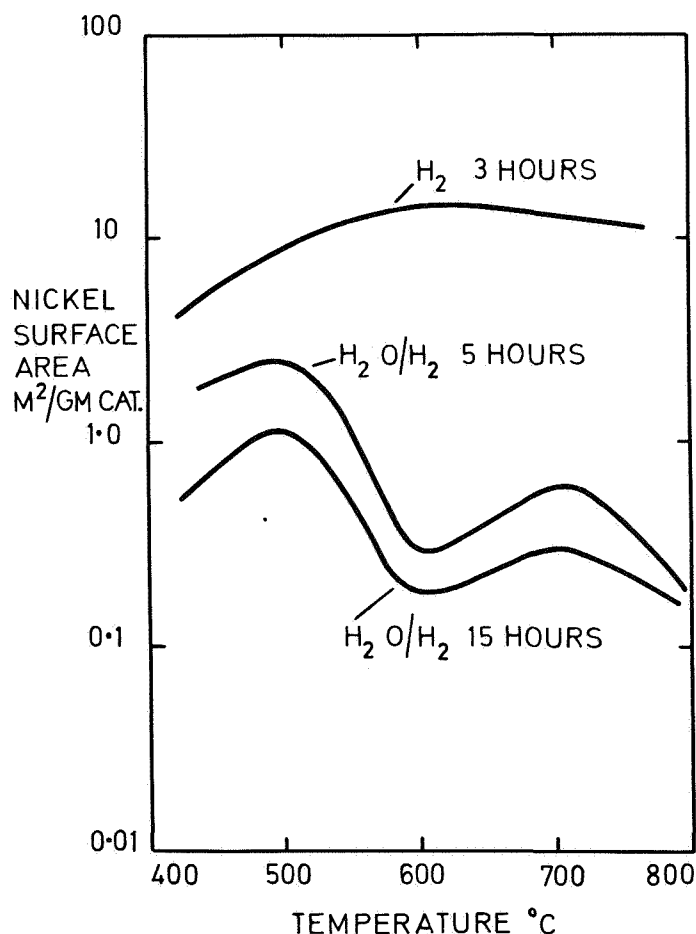


Figure 2. Nickel reduction—precipitated catalyst, 25% Ni ( $H_2O/H_2$ , 8/1 vol.).

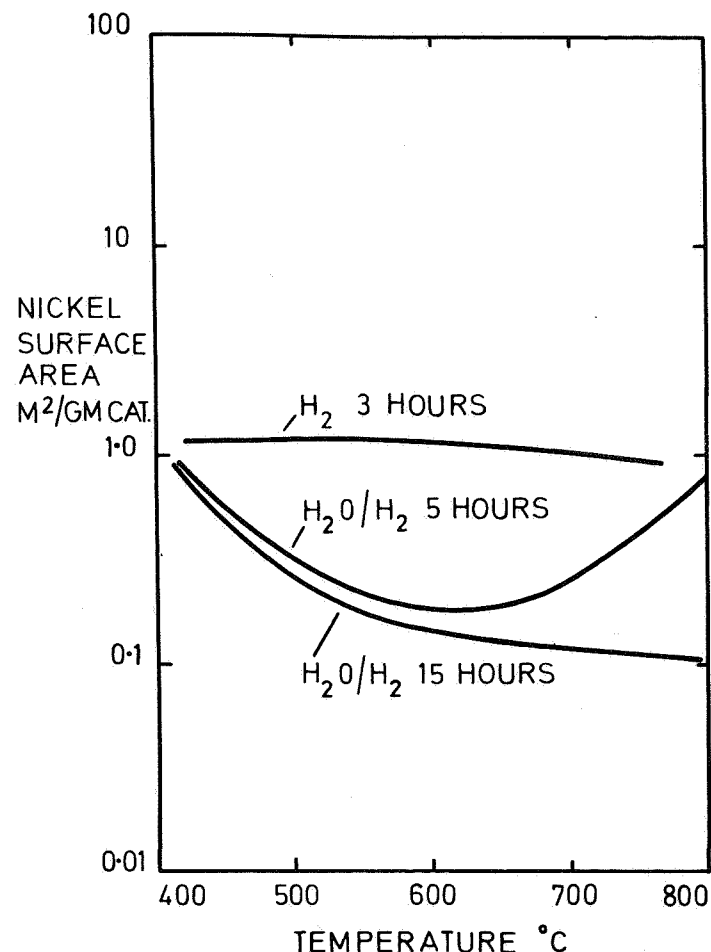


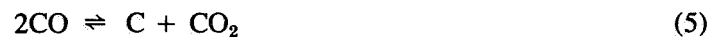
Figure 3. Nickel reduction—impregnated catalyst, 8% Ni on alumina ( $H_2O/H_2$ , 8/1 vol.).

because sintering of the nickel is occurring. When steam is present, lower surface areas are obtained because the sintering process is enhanced, a process which proceeds even further giving even lower surface area as the reduction period is extended to 15 hr.

The shape of the reduction pattern of the precipitated catalyst in the presence of steam with two peaks suggests that the nickel area is derived from more than one nickel compound.

Carbon formation is not normally a problem in reforming natural gas feedstock except in some modern plants operating at high throughput and high heat loading. In such plants, the appearance of "hot bands" after several months' operation probably indicates carbon formation as a result of reduced catalyst activity. (3)

Gas samples taken along the length of a full size reformer tube in a semi-technical plant show that the source of carbon is methane cracking, reaction 4, not CO disproportionation, reaction 5, or CO reduction, reaction 6:



Data were obtained from the experimental full-scale tube for two catalysts of high and low activity. The value of  $p_{\text{CO}_2}/p_{\text{CO}}^2$  and of  $p_{\text{H}_2\text{O}}/p_{\text{CO}}p_{\text{H}_2}$  calculated from the gas composition at different points in the tube are on the carbon-free side of the equilibria for reactions 5 and 6 along the full length of the tube; hence reactions (5) and (6) are carbon-removing.

The values of  $p_{\text{H}_2}^2/p_{\text{CH}_4}$  are shown in Figure 4, and it is clear that with both catalysts the gas composition in the top part of the catalyst where the methane concentration is high is on the carbon-forming side of the methane-cracking equilibrium 4.

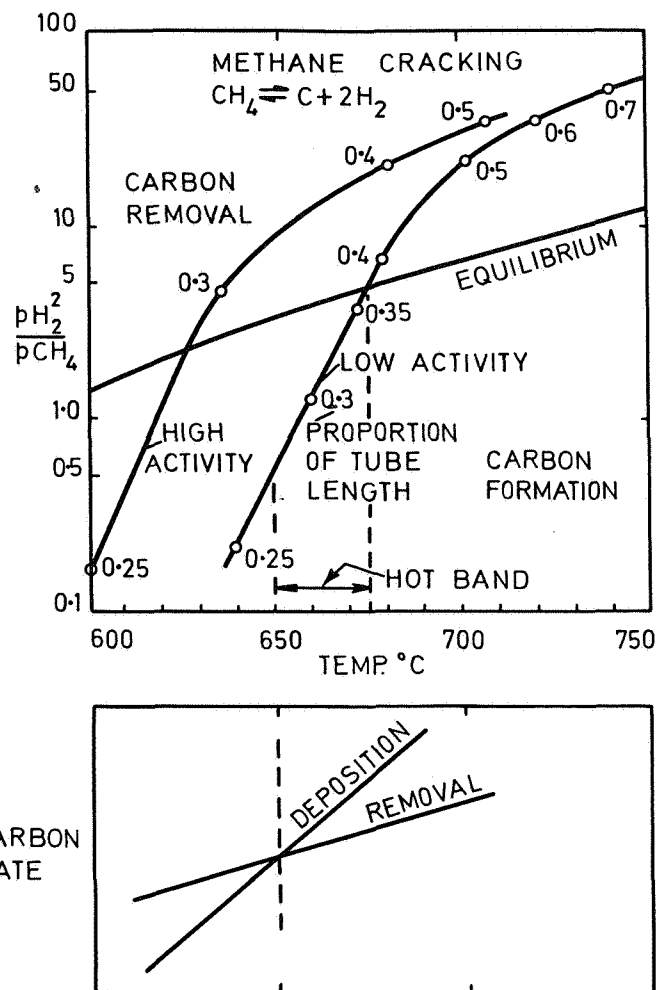
The fact that carbon is not deposited in practice with an active catalyst indicates that the rate of carbon removal by reactions 5 and 6 is greater than the rate of carbon formation by 4.

### Carbon deposition rate may exceed removal

With both catalysts, the gas composition changes to the carbon-free side of equilibrium 4 further down the tube. With the low activity catalyst, this occurs at a higher temperature (*ca* 675°C) than with the high activity catalyst (*ca* 625°C). If the temperature coefficient of the deposition reaction is greater than that of the removal reaction, then it is possible that at some temperature between 625°C and 675°C the rate of deposition will exceed the rate of removal.

This is indicated in the lower part of Figure 4. Carbon will be deposited, but the deposition will cease even with the low activity catalyst, when the gas composition changes to the carbon-free side of equilibrium. Carbon will therefore be deposited over a short length of the catalyst about one-third of the way along the bed, as shown in Figure 4. It will hinder reforming and reduce heat transfer so that the tube wall temperature will rise in that zone, producing a "hot band."

A hot band can result from the decline in performance due to sintering of a catalyst which had high activity



**Figure 4. Methane reforming. Carbon deposition and hot band formation.**

when first put into service. Sintering is permanent, and "hot bands" are only temporarily eliminated by steaming off the carbon. High activity is therefore important in ensuring carbon-free operation and requires a stable catalyst formulation.

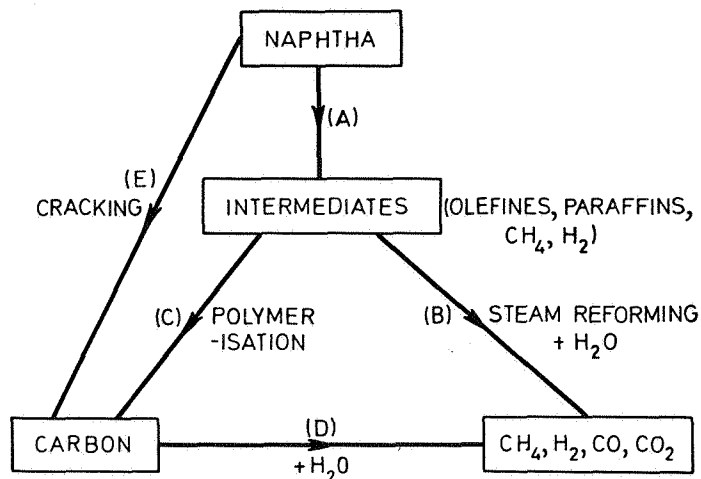
Increased activity in the earlier stages of reforming is obtainable to some extent by using catalyst of a smaller size at the top of the reformer. Smaller catalyst rings provide a greater geometric surface area per unit volume of reactor and make more effective use of the catalyst solid, and also improve heat transfer.

Hydrogen recycle in the reformer inlet feed is beneficial in preventing or delaying the onset of hot bands. It retards the methane cracking reaction 4 and therefore helps to offset the decline in catalyst activity. It can also improve activity by ensuring that the catalyst at the inlet of the reformer is in the reduced state.

### Lighter hydrocarbons increase carbon problem

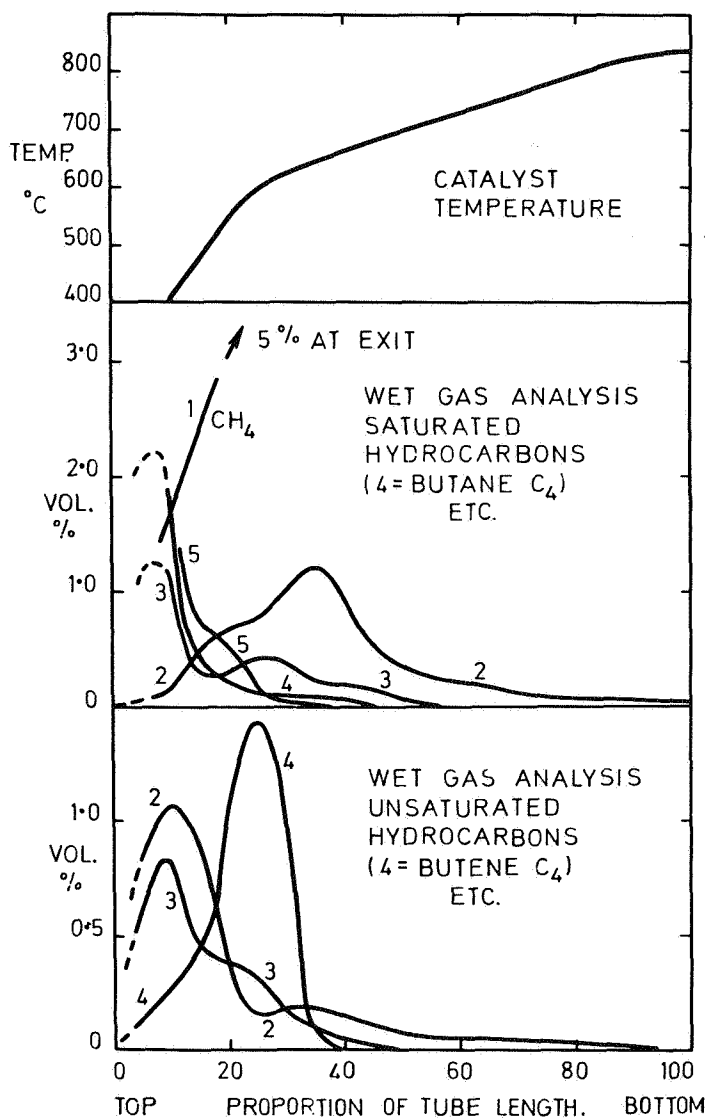
Carbon formation is a bigger problem when the higher hydrocarbons such as naphtha or light distillate are used as feedstock. The overall reaction of the hydrocarbon is expressed by equation 1 but takes place in several successive stages and can follow parallel routes. The mechanism of the reforming process has been discussed by Schnell, (4) and by other workers (1, 5, 6, 7, 8, 9). Schnell's description in simplified form is given in Figure 5.

The initial deposition *A* takes place catalytically above



**Figure 5. Naphtha reforming (simplified). Production of gas and of carbon.**

500°C and thermally above 650°C, producing intermediates consisting of olefins and saturated hydrocarbons of low molecular weight. This initial reaction involves dehydrogenation and demethanation (cracking). These intermediates then react with steam catalytically *B* to produce the product gas of composition defined by the



**Figure 6. Naphtha reforming. Temperature and intermediate concentrations.**

equilibria 2 and 3. The intermediates, depending on their concentrations on the catalyst surface, can also polymerize and dehydrogenate *C* to produce "carbon." Another form of carbon can be produced directly by catalytic or thermal cracking *E* of the feedstock. Carbon produced by either route can react with steam or  $\text{CO}_2$  *D* to produce  $\text{CO}$  and  $\text{H}_2$ .

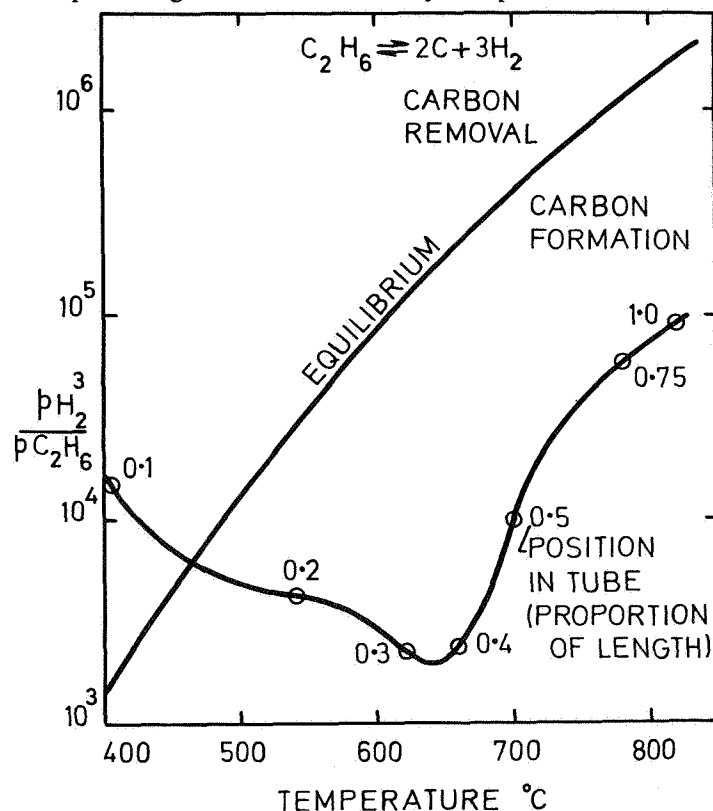
Whether carbon is laid down depends, as in the methane reforming case, on the rates of the carbon-forming and carbon-removing processes. In the naphtha case, there are other carbon-forming mechanisms, *C* and *E*, which have to be considered as well as the simple reactions 4, 5, and 6.

The concentration of the intermediates is a critical factor. Their presence is demonstrated in small scale experiments at short residence time. (4, 10) They can be detected in the gas stream in experiments with a full-scale reformer tube, Figure 6. The significance of, for example, ethane in the gas is illustrated in Figure 7 which indicates that the gas is on the carbon-forming side of the ethane-cracking equilibrium over most of the catalyst.

Thus a reforming catalyst is required to be active both for the initial decomposition of the feedstock and for the steam reforming of the intermediates; at the same time it should have low polymerization activity. Whether a particular catalyst system will or will not form carbon depends upon a delicate balance of these activities and, as in methane reforming, upon the rate at which carbon is formed relative to its removal by reverse reactions 5 and 6.

#### Potash most effective alkali to use

The most successful solution to the carbon problem, one providing the widest flexibility of operation, has been



**Figure 7. Naphtha reforming. Ethane-carbon equilibrium.**

to use a nickel catalyst containing an alkali; potash being particularly effective. The potash neutralizes the acidity of the support and depresses the rate of carbon formation by polymerization, and it accelerates the rate of carbon removal by steam. Catalyst 46-1 containing potash, which was successfully introduced by ICI 15 years ago, (11, 12) will operate for several years without forming carbon.

Other systems, using catalysts containing no alkali or only low concentrations, have been developed and used at full-scale to a limited extent. By very careful catalyst formation and reformer design giving good control of temperatures throughout a reformer, it is possible to achieve the delicate balance referred to earlier between carbon formation and removal. Systems of this sort have reduced flexibility of operation, and changes in reformer firing pattern or temperature profile can disturb the balance and give rise to carbon.

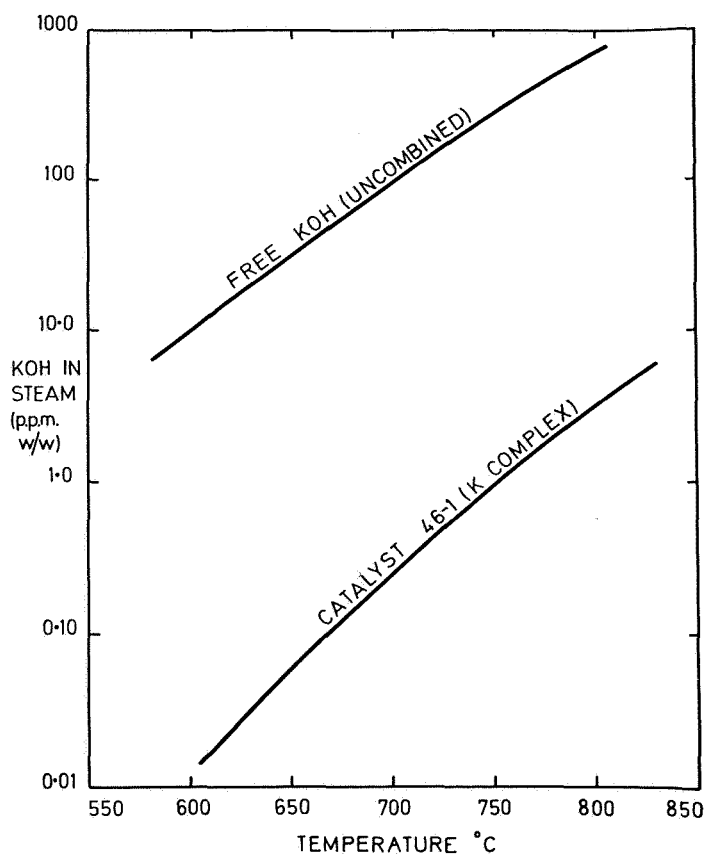
Changes in the catalyst can also occur with time, as with the methane reforming catalyst. This is particularly true with catalysts based on alumina supports containing only small amounts of potash (below 0.5%  $K_2O$ ); the alkali is not combined in the catalyst and is lost in a few weeks' operation. The addition of  $U_3O_8$  to this type of catalyst does not prevent the loss of alkali, although it is claimed that  $U_3O_8$  is beneficial as a water activator by adsorption and decomposition of water which promotes steam reforming activity. (13) The addition of alkaline-earth metals such as barium has been suggested; (14) they will neutralize acidity but are much less effective than potash for catalyzing the steam-carbon reaction.

Spinel-based catalysts incorporating  $MgO$  and  $Al_2O_3$  are also effective under certain operating conditions. (15) Catalysts of this type have been studied extensively. (1, 9) Free  $MgO$  is undesirable, as it hydrates in steam at temperatures below 400-500°C at operating pressures which can cause catalyst disintegration, and it is restricting in practice during start-up and shut-down of plants.  $MgO$  can also give rise to solid solutions with  $NiO$  which are difficult to reduce, as described earlier. The tolerance of these catalysts to low steam/carbon ratios can be increased by the addition of alkali but again the alkali is not retained for many weeks.

### Wide tolerance shown by new catalyst

The ICI naphtha reforming process uses a catalyst, 46-1, containing several percent of  $K_2O$  for the initial decomposition of the naphtha. It provides a wide tolerance to variations in operating conditions in full-scale plants without forming carbon. The potash is evolved from the catalyst but only at a slow rate because it is combined as a complex potassium alumino-silicate (e.g. kalsilite,  $K_2O \cdot Al_2O_3 \cdot 2SiO_2$ ), from which it slowly released as  $K_2CO_3$  at reforming temperatures under high partial pressures of steam and  $CO_2$ .

Magnesia and  $CaO$  take its place in the alumino-silicate forming stable, non-acidic compounds such as gehlenite ( $CaO \cdot Al_2O_3 \cdot SiO_2$ ) and montecellite ( $CaO \cdot MgO \cdot SiO_2$ ). The released  $K_2CO_3$  is hydrolyzed as fast as it is formed, producing  $KOH$ , which is volatile and mobile on the catalyst surface and is the effective carbon-removing agent. The  $KOH$  is therefore slowly lost from the catalyst but only at a very low rate, kinetically controlled by the



**Figure 8. KOH concentration in steam (slow evolution from K-complex in Catalyst 46-1). Total pressure 40 atm.**

decomposition of the kalsilite compounds; and the concentration of  $K_2O$  in the exit steam is much lower than the vapor pressure of free  $KOH$ , as seen in Figure 8.

The effectiveness of the slow-potash-release catalyst 46-1 has been established by experience in many plants over the last 15 years. The catalyst can operate at a steam ratio of 3.0, about 1.5 above the theoretical minimum for periods of several years over a wide range of operating conditions with hydrocarbon feedstocks boiling up to 220°C.

The potash is only essential in the inlet half of the catalyst bed where the concentration of unsaturated intermediates, as shown in Figure 5, produced by the initial decomposition of the feedstock can rise to critical levels, seen in Figure 6.

The lower half of the catalyst bed need not contain potash, although the catalyst now used there, 46-4, had to be especially formulated to avoid high acidity and to achieve high reforming activity. The highest temperatures occur in this part of the bed, shown in Figure 6. By using potash-free catalyst there, the rate of evolution of alkali from the reformer as a whole can be kept at a very low level.

A higher overall activity is obtained by using the two-bed, 46-1/46-4 system, which gives a lower exit methane concentration or enables the catalyst temperature to be lowered. For example, the methane content of the product gas from a reformer producing hydrogen at 15 atm. pressure can be reduced from 2.8% with 46-1 alone to 1.2% with the two-bed system, or the reformer can be operated at 50-60°C lower temperature.

## Conclusions

The formulation of a good reforming catalyst is complex because of the conflict between its important characteristics such as high activity, metal content, sintering, etc. The choice of components required to give strength and stability is restricted because they must not make the catalyst difficult to reduce or give rise to carbon formation. The catalyst manufacturer is continually researching to meet these requirements.

Today the importance of high activity in avoiding carbon formation and hot tubes in methane reformers is becoming more apparent. In naphtha reforming, where the carbon problem is more acute, the best solution is obtained with a catalyst system containing potash which provides the greatest safety margins on the plant.

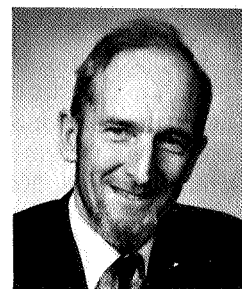
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G.W. Bridger

## DISCUSSION

**Q.** It would seem that there could be some practical advantages to a spherical reforming catalyst. Has ICI given any consideration recently to changing the form?

**BRIDGER:** Our catalysts are conventionally of the Raschig ring type with a hole in the middle. We have thought about spherical catalysts from time to time. They can facilitate charging of the reformer tubes as they can pack more uniformly, but they can also be more difficult to make in uniform sizes and uniform shape. They could have high pressure drop and we don't really think that there are advantages to be obtained from a spherical catalyst.

**Q.** Would it be possible to utilize a naphtha reforming catalysts in solving the hot bands problem and has there been any experience with that?

**BRIDGER:** Yes there is this possibility of using an alkalis catalyst for methane reforming, but as I commented at the end of my paper, alkali does depress the activity of the reforming catalyst for methane. Therefore you have a choice: you can put alkali in and thereby possibly prevent carbon formation, but at the cost of losing

some activity of the catalyst which might mean a larger reformer and a larger catalyst volume. One might be able to use an alkalis catalyst in selected parts of reformers but this is a further complication for plant people to keep the catalysts separate. We have top and bottom catalysts and if another catalyst has to go in, shall we say, the second quarter of the tube, I don't think it would be practicable. I say the second quarter of the tube because that's the area as I indicated in one of my diagrams, where the carbon formation is the biggest problem and where hot bands occur.

**JOHN LIVINGSTON, ICI, Birmingham:** This question of recycle hydrogen is quite the hardy annual. There was a plant, I think at Bristol, where because of production reasons the hydrogen recycle was stopped for several days. At the end of that period there were signs that hot bands were beginning to appear in the reformer. As the hydrogen was restored after the three or four days, we again saw removal of the hot bands. So there is definite evidence that recycled hydrogen can, in fact, control and, indeed, reverse the carbon formation situation.

**BRIDGER:** I don't think I can add much to that, John. As I said in my paper, it is our experience that hydrogen recycle is beneficial, and worth doing even at some cost. We showed that carbon formation by methane cracking can be reversed, and so we try to maintain up to about 5% recycled hydrogen in our methane reformers. It's a distinct benefit we believe.

**ANDERS NIELSEN,** Haldor Topse A/S: I would like to make a few comments to your presentation. In your paper you say that there are other steam naphtha reforming systems using catalysts containing no alkali or only low concentrations, which are used on a full scale to a limited extent and in your discussion, if I am quoting you correct, you added "under certain limited reforming conditions".

To this I would like to say that there are indeed. We have licensed about 25 industrial units of which the first started up in the 60's and of which some have experienced a catalyst life in excess of four years on naphtha. These units are operating at a very wide range of conditions. Between them are a couple of Towns Gas plants, a few ammonia plants of which two are of a capacity of 1000 MTPD each and operate at a steam to carbon ratio of 3.5 on full range naphthas. Many of the applications are hydrogen plants with higher steam to carbon ratios. Some of these units operate at a pressure up to 600 psig. at reformer inlet.

In your summary you mention that catalyst systems which depend on magnesia rather than potassium oxide to prevent carbon formation in the catalyst are subject to hydration below 500°C. That figure should have been 360°C, and as a matter of fact, some of the reformers are operating with an inlet temperature below 500°C.

You discussed in quite some detail the question of the formation of mixed oxides of magnesium oxide and nickel oxide and the difficulty of reducing nickel out of the mixed oxides. Now, the answer to that, of course, is to supply a pre-reduced catalyst as we are doing. In your paper you also mention that the ICI steam naphtha reforming process uses catalyst containing several percent of potassium oxide and that this potassium is combined in a complex potassium aluminosilicate. That means your catalyst contains silica as well as alkali and I wonder whether you or John Cromeans would like to make any comments to this.

**BRIDGER:** I will deal with those four points, in order. Referring to the reformers that are running with a non-alkalised catalyst, I think Dr. Nielsen has made my point in that he says most of them are hydrogen plants which, of course, are running at high steam ratios in order to get the low methane content.

As regards the temperature of operation of catalyst containing magnesia, I was referring to the temperature during startups and shutdowns rather than operating temperature. If the plant has an emergency then with free magnesia in the catalyst one has to be very careful to get the steam off at some temperature, (thermodynamically it is 500°C but in practice may be about 360°C) to avoid catalyst disintegration.

Dr. Nielsen agrees with me that magnesia does affect the reduction of nickel because of the formation of solid solutions. As he says this can be overcome by using a pre-reduced catalyst but then there comes the time when

the plant shuts down and of course the nickel is re-oxidized and then may form solid solutions again. Then reduction can be difficult.

On silica, I have not a great deal of comment. It's not used in methane reforming catalysts where silica evolution at high pressure, is a real problem. We did many experiments 15 years ago when we were first working on our alkalised naphtha reforming and showed that silica evolution was not a problem there because it was combined in the catalyst and made a stronger catalyst. The experiments established that at 850°C, steam partial pressures of the order of 20 atmospheres, quite a high concentration of silica comes out of a methane reforming catalyst containing uncombined silica. This is particularly true of high temperature secondary reformers. And this silica is obviously a nuisance when it gets into boilers and onto HT shift catalysts downstream. I feel the customer is right in insisting on a low silica catalyst for methane reforming.

**NIELSEN:** One small comment to what you say about reduction of a magnesia-containing catalyst. It is true what you mention that when you shut down the plant, you may form some nickel oxide. Now I think you will agree with me that because you form some nickel oxide you do not necessarily form the types of solid solutions which are quite difficult to reduce.

**BRIDGER:** Yes, you may be right but with free magnesia there is always the possibility of solid solution formation.

**Q.** I want to refer to your last slide, and the case for making hydrogen. Your design is relatively conservative: 15 atmospheres and 800°C exit temperature, and in order to achieve the desired low methane content you use a fairly high steam ratio. Probably you do this because you have alkali in the catalyst and do not want to exceed about 800°C because of the carry over of alkali. Wouldn't it be better when using naphtha for hydrogen generation, to make a so-called rich gas with a high methane content in a first step on a nickel catalyst in an autothermic way, at about 400°C. And as a second step, then reforming that gas at an outlet temperature of about 860° or 870°C even at about 80(?) atmospheres pressure. In this way you could reach about 2% residual methane content, and use an overall lower steam ratio.

**MAX APPL,** BASF, Germany: I want to refer to your last slide, and the case for making hydrogen you have shown here. From the standpoint of tube material, your design is relatively conservative, 15 atmospheres and 800 degrees centigrade gas temperature at the outlet, and you achieve the desired low methane content by using a fairly high steam to carbon ratio. Probably you do so because you have alkali in your catalyst and in that case you don't want to exceed about 800 degrees centigrade in order to prevent the carry over of alkali. Wouldn't it be a better approach to make a so-called rich gas step, in which you transfer the naphtha with steam on a nickel catalyst in an autothermic way, at about 400 degree centigrade to a gas with a high methane content. As a second step, then conservatively make a gas reforming and in this case you can then go to outlet temperatures of about 860 or 870 even at about 20 atmospheres pressure and so also reach about 2% residual methane content, using an overall lower steam ratio.

**BRIDGER:** Yes, that is another way of producing hydrogen, by converting the naphtha into methane which can then be reformed. But this is then a two-stage process which is inexpensive and I believe in terms of economics, taking into account capital costs as well as running costs, it is still best and cheapest to do it the way which we are recommending. And obviously, one runs at the highest steam ratios and rather low pressures in order to get the lowest methane content. We still think the single stage process is the best way to get hydrogen gas of low methane content.

**Q.** I'd like to ask a question about this hydrogen recycle.

It's been reported that some people have tried it and encountered hydrogen blistering. Would you care to comment on that?

**BRIDGER:** I don't feel really able to comment about that metallurgical problem. Perhaps my friends from ICI could comment on that. Relative to the catalyst performance we have found hydrogen is beneficial for removing carbon and in our experience has had no deleterious effect on tubes. We've been running our reformers with hydrogen recycle for the last three years, I should think at least, and it has had no bad effects.