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Deactivation of copper-based catalysts for fuel cell applications

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The activity of copper catalysts for the steam reforming of methanol was investigated under deactivating conditions. The effects of adding poisonous substances which can occur in the fuel, such as sulphur and chlorine, were studied. Thermal ageing by sintering was observed while exposing the catalyst to high temperatures. The catalyst activity for steam reforming was greatly affected by the addition of low concentrations of sulphur and chlorine. Sulphur was more detrimental to the catalyst than chlorine.

KEY WORDS: deactivation; poisoning; copper catalyst; sulphur; chlorine; fuel cell; methanol reforming

1. Introduction

1.1. Background

Fuel cell vehicles have been investigated for several years as an alternative to the combustion engine. For a fuel cell vehicle to match the high performance of modern automobiles a fast and highly responsive supply of hydrogen with no by-products other than CO_2 must be found. The high selectivity requirements emanate from the sensitivity of the polymer electrolyte membrane (PEM) fuel cell [1,2], which is easily deactivated when carbon monoxide is introduced. The overall performance of the reformer system is dependent on the ability to produce a catalytic system with a stable operation window. The stability of the catalyst can be seen as its ability to withstand deactivation.

The steam reforming of methanol is described by the following equation:

$$CH_3OH + H_2O \rightarrow 3H_2 + CO_2$$

The maximum theoretical hydrogen content in the product stream is 75% on a dry basis. Deactivation will not only produce undesirable by-products, but it will also lower the hydrogen content in the product stream. In fuel cell applications this will lower the Nernst potential and consequently the performance of the fuel cell.

1.2. Catalyst activation

The activation of a catalyst can be seen as the final step in the production of a catalyst [3]. The activation process, however, is almost always carried out by the end user rather than by the catalyst manufacturer.

The manner in which the activation procedure of the catalyst is carried out is dependent on the nature of the catalyst, the application and the specific process requirements, such as the tolerance for various by-products. The traditional catalysts used in methanol reforming are supported metals and during the reduction process the activation takes place by reduction of metal oxides into fine metal crystals. Hence, the active sites will be made up of the metal crystals [3].

The main reasons for carrying out the activation of copper-based catalysts on site are:

- The reduced metal crystals are sensitive to oxygen.
- A correct activation method is important so that the activated catalyst meets the various process demands set by the end user.
- The activated catalyst can easily be contaminated during transportation and installation.

2. Experimental

2.1. Catalyst description

A commercial catalyst G66-B, a $Cu/ZnO/Al_2O_3$ catalyst from Süd Chemie, has been tested in this experiment for the steam reforming of methanol. The catalyst was in the form of pellets and 15 g was used in all of the experiments. In order to activate the catalyst, the copper oxide was reduced to copper crystals in the reactor using a mixture of 10% hydrogen in nitrogen prior to the experiments. The reduction was performed at a temperature interval between 180 and 300 °C at a rate of 2 °C/min.

2.2. Experimental conditions

The experiments were performed in a fixed-bed reactor and the reactants were vaporised prior to entering the reactor. The experiments were carried out over a temperature interval of 180–350 °C. The molar ratio of water to methanol

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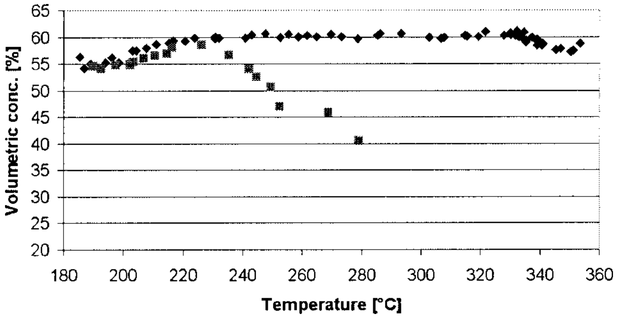

Figure 1. Hydrogen concentrations (dry gas): (♦) %H_2 (fresh catalyst) and (■) %H_2 (temp.-deactivated).

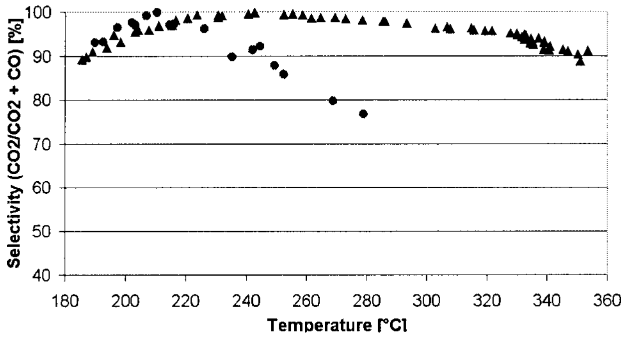

Figure 2. CO_2 selectivity: (▲) G66B (fresh catalyst) and (•) G66B (temp.-deactivated).

was 1 : 1 for the experiments. In order to achieve steady-state conditions measurements were taken 10 min after the reactants had entered the reaction chamber. The product gas was measured on-line with a gas chromatograph from Varian equipped with both FID and TCD detectors.

2.3. Methods of deactivation

In the thermal deactivation experiments (see figures 1 and 2) the fresh catalyst was heated to 350 °C under steam reforming conditions. The catalyst was kept at 350 °C for a period of 2 h. Subsequently the catalyst was cooled in nitrogen atmosphere in the reactor and the steam reforming experiment was repeated. In the poisoning experiments the respective impurities were added to the catalytic system. The sulphur was added in the form of sulphuric acid (H_2SO_4), with a concentration of 2 ppm (w). The chlorine was added as chlorite (ClO_2^-), which is often used to purify water, at a content of 5 ppm (w).

3. Results

3.1. Effects of sintering

The results from temperature deactivation compared to a fresh catalyst are presented in figures 1 and 2. The exposure of the catalyst to temperatures above 340 °C causes a loss of catalytic activity. The CO_2 selectivity is also decreased when the catalyst is subjected to high temperatures.

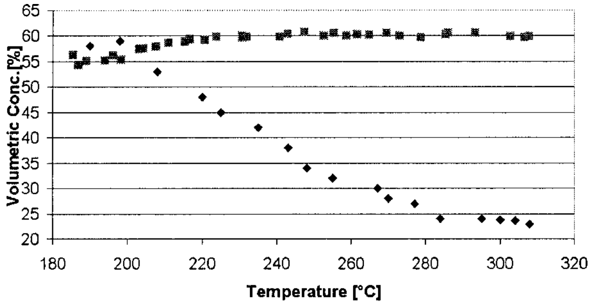

Figure 3. Hydrogen concentrations (dry gas): (♦) %H_2 (S-deactivated) and (■) %H_2 (fresh catalyst).

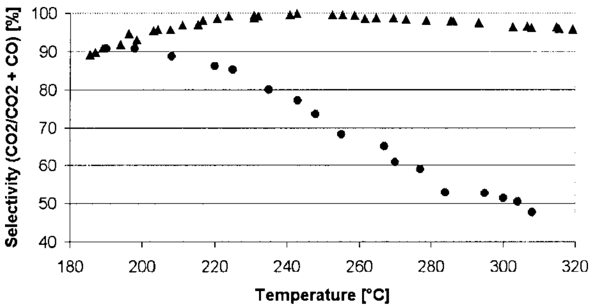

Figure 4. CO_2 selectivity: (▲) G66B (fresh catalyst) and (•) G66B (S-deactivated).

3.2. Sulphur poisoning

In figures 3 and 4 the effects from the addition of 2 ppm (w) sulphur to the methanol is presented.

The effects of the addition of sulphur were devastating for the performance of the catalyst (see figure 3). The selectivity was also lowered considerably (see figure 4). The powerful impact of the sulphur makes it imperative that any contact between the catalyst and sulphur must be avoided.

3.3. Chlorine poisoning

The impact of chlorite, ClO_2^-, on the catalyst is shown in figures 5 and 6.

The addition of chlorite to the system followed the same trends as with the sulphur. However, although the deactivation effects were considerably lower than for sulphur the resultant activity is far below accepted levels.

The catalyst response to the foreign substances was also tested for a longer time interval at a constant temperature, 220 °C, and the results of this are presented in figure 7. The catalysts were deactivated to the same degree at the lower temperature as they were for the entire temperature span presented earlier. As a comparison the time dependency of the sintering is also presented in figure 7.

4. Discussion

4.1. Physical deactivation

When the reduced copper catalyst is exposed to temperatures above 350 °C a significant decrease in catalyst activity

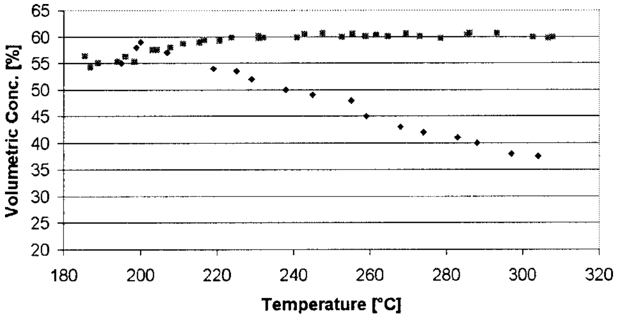

Figure 5. Hydrogen concentrations (dry gas): (◆) %H_2 (Cl-deactivated) and (■) %H_2 (fresh catalyst).

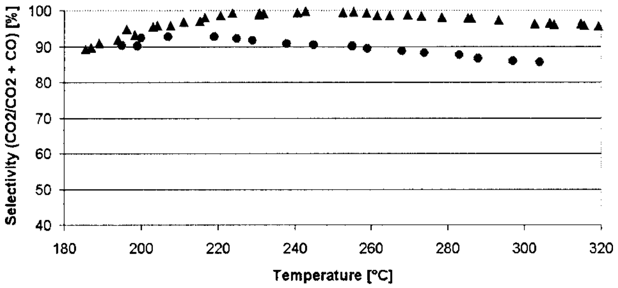

Figure 6. CO_2 selectivity: (▲) G66B (fresh catalyst) and (•) G66B (Cl-deactivated).

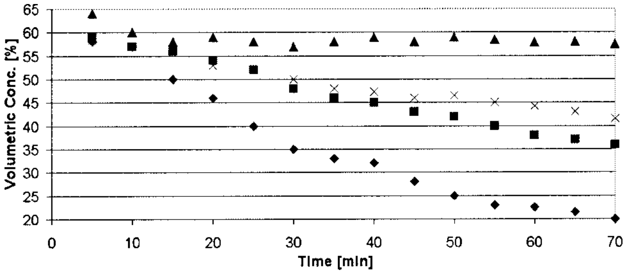

Figure 7. Time dependency of deactivation at 220 °C: (◆) %H_2 (S-deactivated) and (■) %H_2 (Cl-deactivated), (▲) %H_2 (fresh catalyst) and (×) %H_2 (temp. deactivated 350 °C).

is observed. The catalyst has been prematurely aged and the surface properties have been modified. A physical description is that large blocks of active material have been formed [3]. This kind of reduction of surface area is called agglomeration of crystals, and it causes a loss of surface area. The agglomeration is an irreversible process and decreases the catalyst activity (*cf.* figure 1).

The activity observed for a fresh $Cu/ZnO/Al_2O_3$ catalyst will, after initialisation, decrease to a stable level after some operating time. The time required for a catalyst to stabilise can vary depending on the catalytic material used (*cf.* figure 7).

4.2. Chemical deactivation

Catalyst surfaces usually contain several active sites, however, only a few active sites are involved in the catalytic process. This implies that a small amount of poison can do a large amount of damage to a catalyst. A reaction between a catalyst and poison does not necessarily render the catalyst totally inactive. It can also form a new compound, which has a lower activity than the original surface. The loss of activity is seldom instantaneous; it is rather a continuous process.

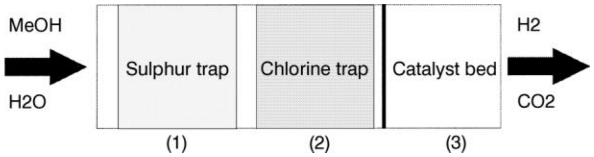

Figure 8. Reactor with trap for poisons.

Sulphur is a common impurity in syngas, which is the primary raw material for the world production of methanol. The sulphur can occur as hydrogen sulphide (H_2S), thiophene (C_4H_4S) and carbonyl sulphide (COS). The presence of sulphur affects both the production of methanol (since similar catalysts are often used) and the steam reforming. Extremely sensitive to sulphur is the ZnO molecule on the catalyst [4,5], which reacts with ease to form ZnS and/or $ZnSO_4$. A probable mechanism for the deactivation by sulphur is [4,6]

$$ZnO + H_2S \rightarrow ZnS + H_2O$$

Since sulphur primarily affects the ZnO dispersion properties one can assume that the higher the ZnO content the lower impact the sulphur will have on the catalyst activity.

Chlorine is not usually considered a problem since there have not been reports of chlorine in methanol. However, when the reforming system is to be used in automobiles, the process water will most probably not be deionised water and in many countries, especially third-world and heavy industrialised countries, chlorine is used as a the primary disinfectant of water. If chlorinated water comes in contact with the catalyst several problems will arise. The most prominent is that of the formation of volatile copper chloride compounds, which will produce high deactivation effects and thereby render the catalyst useless (*cf.* figures 5 and 6).

4.3. Solution to the poisoning problem

To prevent the sulphur and chlorine to reach the catalyst the following steps can be taken.

By placing traps for the poisons it is possible to prevent the catalyst deactivation from taking place. Since ZnO reacts so easily with sulphur, it would seem obvious that placing an appropriate amount of ZnO prior to the catalyst would be an effective method of removing the sulphur from the gas stream. It has been reported [3] that chlorine reacts efficiently with active aluminium oxide. Therefore, by placing the aluminium oxide before the catalyst the chlorine problem can be solved in the same manner as the sulphur. Figure 8 illustrates the solution described above:

(1) sulphur trap (zinc oxide);

(2) chlorine trap (aluminium oxide);

(3) fully active reforming catalyst.

4.4. Secondary poisoning effects: fuel cell applications

Catalyst poisoning by reaction products is a common problem when dealing with higher hydrocarbons as soot formation causes loss of catalyst activity. However, this is not a problem when reforming methanol, as there is only one carbon atom in each molecule. For the steam reforming of methanol the most prominent problem with the reaction products is the formation of carbon monoxide. The formation of carbon monoxide is especially a problem when the reforming system is integrated with a fuel cell, which is ultrasensitive to carbon monoxide. However, by increasing the H_2O/CH_3OH ratio it is possible to induce the water–gas shift (WGS) reaction in which the undesired carbon monoxide reacts with water to produce carbon dioxide and hydrogen.

5. Conclusions

- The resulting deactivation of the commercial catalyst performed in this study indicates clearly that caution must be taken in order to prevent any contact with either chlorine or sulphur, as the deactivation is detrimental to the catalyst.
- Temperature control is also of high priority when reforming methanol over this kind of catalyst as the contact with excess heat physically deactivates the catalyst.

Acknowledgement

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References

[1] S. Thomas and M. Zalbowitz, Report No. LA-UR-99-3231, Los Alamos National Laboratory, NM (1999).

[2] J.C. Amphlett, R.F. Mann and B.A. Peppley, Int. J. Hydrogen Energy 21 (1996) 673.

[3] M.V. Twigg, ed., *Catalyst Handbook*, 2nd Ed. (Wolfe, London, 1989).

[4] D.L. Trimm, in: *Handbook of Heterogeneous Catalysis*, Vol. 3, eds. G. Ertl, H. Knözinger and J. Weitkamp (VCH, Weinheim, 1997) ch. 7.

[5] S.G. Abens and G. Steinfeld, in: *Proc. 32nd Intersoc. Energy Conv. Eng. Conf.* (1997) p. 851.

[6] L.J. Pettersson and R. Westerholm, Int. J. Hydrogen Energy 26 (2001) 243.