Activity and durability of water-gas shift catalysts used for the steam reforming of methanol

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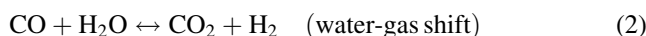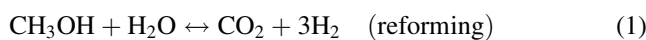*IdaTech, LLC, P.O. Box 5339, Bend, OR 97708, USA*

Abstract

Commercially available water-gas shift catalysts were tested for methanol steam reforming in small-scale packed bed reactors at atmospheric pressure. The results showed that while the initial activity of chromia or zinc oxide catalysts was lower than that of copper-based catalysts, the durability of the chromia preparations was far superior to that of the copper-based samples at the temperatures investigated. Kinetic modeling suggested that copper and zinc oxide catalysts have deactivated by sintering of the metal phase; instead, the deactivation of chromia catalysts is consistent with feed poisoning. A zinc oxide/chromia catalyst was among the most active, and it certainly was the most stable, catalyst tested.

1. Introduction

Methanol reacts with steam in the presence of copper-based materials at temperatures higher than 160 °C to form a hydrogen-rich gas. The main products are H_2, CO_2 and CO. The formation of methane is thermodynamically favored, but copper catalysts usually do not promote the formation of this by-product. Hence, the process can be described by the following three reactions:

$$CH_3OH + H_2O \leftrightarrow CO_2 + 3H_2 \quad \text{(reforming)} \quad (1)$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \text{(water-gas shift)} \quad (2)$$

$$CH_3OH \leftrightarrow CO + 2H_2 \quad \text{(decomposition)} \quad (3)$$

Commercial water-gas shift catalysts are used for methanol steam reforming because they facilitate reactions (1) and (2). At the high methanol conversions found in steam reformers the rate of CO formation is controlled by the rate of reaction (2), while the rate of the decomposition reaction (3) is considerably smaller than the rate of the other two reactions; therefore, the concentration of CO in the reformer effluent is lower than that predicted from thermodynamic equilibrium calculations for methanol/steam mixtures [1].

Methanol steam reforming on copper-based water-gas shift catalysts has been extensively studied in the literature [1,2]. In the present report, we examine the activity and durability of selected commercial water-gas shift catalysts and make recommendations for choosing catalysts for methanol fuel processors.

2. Experimental

The vaporizer and reactor unit shown in Fig. 1 was machined from a 6 in. long stainless steel cylinder 1.25 in. diameter. Two holes were drilled down the length of the cylinder for heater cartridges to provide heat for the reforming reaction. Two 0.25 in. i.d. holes were drilled nearly the length at 90° angles to the heater cartridge holes. One passage was filled with stainless steel wool and the other one with catalyst. The catalyst and vaporizer passages were connected internally by a 0.25 in. i.d. channel perpendicular to the passages. A thermocouple inserted in the channel connecting the vaporizer and reactor sections was used to measure and control the reactor temperature. Catalyst samples were crushed, sieved and weighed prior to loading in the reactor. Particle sizes between 30 and 35 mesh (0.5 and 0.6 mm) were used in all tests.

A mixture of 64% by weight methanol (Fisher, ACS Grade) in water (14 Mohm, in-house DI) was prepared for

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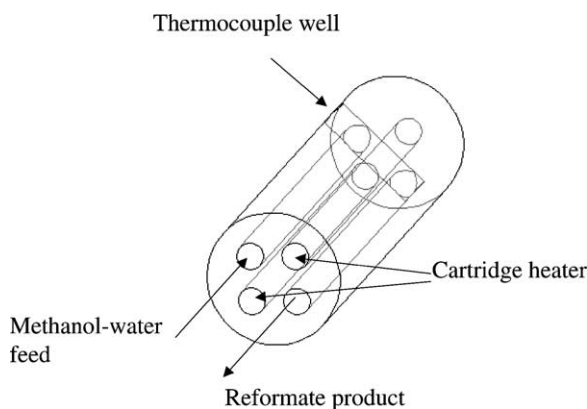*E-mail address:* dloffler@idatech.com (D.G. Löffler).

Fig. 1. Sketch of the vaporizer and reactor unit.

steam reforming reactions. This liquid feed was metered to the vaporizer/reactor assembly by an HPLC pump capable of controlling feed rates in the range from 0.1 to 4 ml/min. The methanol/water mixture entered the bottom of the vaporizer/reactor assembly and flowed upwards through the vaporizer channel and downwards in the catalyst-packed passage. The effluent from the reactor was passed through a condenser to remove unreacted methanol and water; then the dry product gas was sampled into a gas chromatograph. Methanol conversion was calculated from the difference between the volumes of methanol/water mixture fed and the unreacted methanol and water recovered in the condenser. The relative amounts of hydrogen, carbon monoxide, methane and carbon dioxide in the reformer effluent were obtained from the gas chromatograph analysis.

Water-gas shift catalysts were tested using an equimolar solution of methanol and water fed at flow rates between 2 and 4 ml/min. The catalyst samples used weighed between 6 and 9 g and the reactor temperatures varied between 250 and 500 °C. Catalyst composition and operating conditions are detailed in Table 1. The reactor operated around the clock; in some cases, temperatures were periodically cycled to room temperature to simulate service in a fuel processor operated intermittently.

3. Equilibrium calculations

The possible reactions between methanol and water can yield as products hydrogen, carbon oxides, methane and carbon. The experimental results in this study indicated that all catalysts except for Sample E produced no detectable amounts of methane, while no carbon deposits were evident from visual inspection of catalyst samples after reaction. Experimental results consistently showed lower CO levels and higher CO_2 levels than those expected from equilibrium calculations for mixtures of methanol, water, hydrogen, and carbon oxides. Table 2 shows a typical reformer effluent composition.

Table 1
Catalyst sample composition and test conditions

Test #	Catalyst sample	Composition	Mass (gm)	Temperature (°C)
1	Sample A	$CuO/ZnO/Al_2O_3$/graphite	8.1	250
2			8.2	300
3			8.2	350
4	Sample B	$ZnO/CuO/Al_2O_3/Cr_2O_3$	6.4	275
5			6.4	300
6			7.5	350
7			6.3	400
8	Sample C	$ZnO/CaAl_2O_4$	7.1	400
9			7.5	450
10			6.8	500
11	Sample D[a]	ZnO/Cr_2O_3	9.5	350
12	[a,b]		9.1	400
13	[a,b]		9.4	450
14	[b,c]		9.3	400
15	Sample E[d]	$Fe_2O_3/Cr_2O_3/CuO$/graphite	6.9	400
16	[d]		6.7	450
17	[d]		6.7	500

Unless indicated otherwise, methanol/water flow rate was 2 ml/min. Pressure was atmospheric.

[a] Cycled to room temperature daily for over 100 days.
[b] Conversion was measured also at 375 °C.
[c] Flow rate was 4 ml/min for the first 960 h, then it was decreased to 3 ml/min.
[d] Methane was formed.

4. Kinetic model

Preliminary data evaluation showed that all catalyst tested decayed with time. In some cases, methanol conversion was stable at values close to 100% for periods of time up to hundreds of hours before decaying, indicating that the catalyst initial activity was high enough that full conversion was obtained at some distance from the reactor outlet. In other cases, the initial activity of the catalysts was not high enough to sustain full conversion; in those cases, methanol conversion levels decayed continuously through the test. Curves of conversion versus time showed two distinct patterns: either an abrupt, rapid decay to very low conversion levels as shown in Fig. 2, or a relatively slow exponential decay to an almost constant lower level. These observations suggested that at least two different deactivation mechanisms are needed to interpret the experimental data; those mechanisms are feed poisoning and metal particle sintering.

A period of catalyst stability followed by a rapid decay in conversion can be interpreted assuming that a feed poison

Table 2
Composition of reformer effluent at 375 °C—Sample D test #13

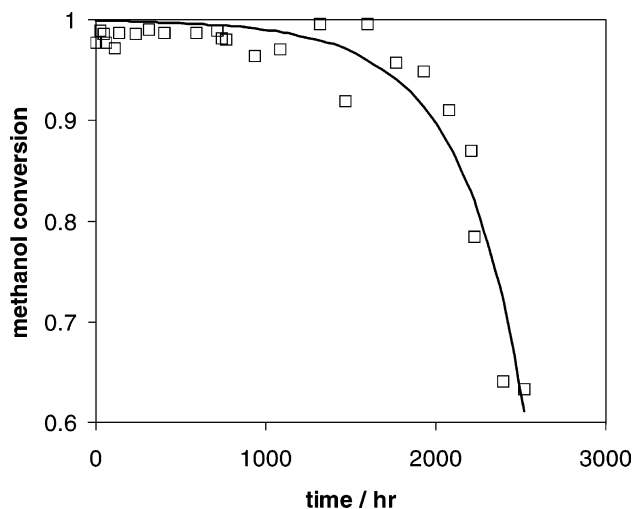|	H_2 (%)	CO (%)	CO_2 (%)
Equilibrium calculations	73	9	18
Measured	74	3	23

Fig. 2. Feed poison deactivation. Methanol conversion vs. time for test #12. Solid line is calculated from Eq. (6) for $k_e = 0.83$ mol/(atm kg h) and $k_{fp} = 0.00036$ h^{-1}.

adsorbs strongly on the catalyst and only becomes evident after the catalyst activity has decayed such that complete methanol conversion is no longer achieved. Alternatively, the active component could be eluted downstream of the reactor inlet. In either case, a zone of inactive catalyst is formed at the inlet of the reactor. As the test progresses, more catalyst is deactivated; hence, the zone of inactive catalyst moves downstream from the reactor inlet. If the reactor contains more catalyst than needed to achieve full conversion when the catalyst is fresh, the conversion at the reactor outlet will not change until the amount of active catalyst left in the reactor is insufficient to fully convert the feed. At this point, the conversion starts to decay abruptly.

A second deactivation mechanism assumes that the activity of the whole mass of catalyst decays uniformly with time on stream. This type of deactivation can be caused by temperature-induced transformations such as metal particle sintering, phase transitions, and metal–support interactions. All these phenomena will result in an exponential decay of catalyst activity with time.

4.1. Model equations

The experiments were designed primarily to compare activity and durability of commercial catalysts under conditions similar to those found in our steam reformers. The limited range of process conditions investigated and the high conversions obtained in most experiments make the data obtained unsuitable for detailed mechanistic interpretations. Yet, a simple kinetic model should suffice to compare activity and durability between the different catalyst samples tested.

4.2. Feedstock poisoning model

A simplified approach to comparing deactivation mechanisms is to assume that reaction (1) is first order irreversible

and ignore reactions (2) and (3) [2]. The rate of reaction is then,

$$r = k_e^0 C_{CH_3OH} \qquad (4)$$

where k_e^0 is an effective first order reaction rate constant and C_{CH_3OH} is the partial pressure of methanol. The units for k_e^0 and C_{CH_3OH} are reciprocal time and concentration, respectively. Introducing (4) in the mass balance equation for a plug-flow reactor we obtain, after some algebra [3],

$$k_e = \frac{F_{methanol}}{W_{catalyst}P_{methanol}}(-2\ln(1 - x_{methanol}) - x_{methanol}) \qquad (5)$$

where $F_{methanol}$ is a molar feed rate, $W_{catalyst}$ the catalyst mass, $P_{methanol}$ the partial pressure of methanol in the feed, and $x_{methanol}$ a fractional conversion of methanol to other species. The units for the effective reaction rate constant k_e are mol/(s kg bar).

When the catalyst is feed-poisoned, the mass of catalyst available for reaction decreases with time at a rate that is proportional to the feed rate and the concentration of poison in the feed. Thus, the mass of catalyst $W_{catalyst}$ in (5) should be a function of time. Eq. (5) can be written as

$$k_e = \frac{F_{methanol}}{W_{catalyst}^0(1 - k_{fp}t)P_{methanol}}(-2\ln(1 - x_{methanol}) - x_{methanol}) \qquad (6)$$

where $W_{catalyst}^0$ is the mass of fresh catalyst loaded in the reactor and k_{fp} the fraction of catalyst deactivated per unit time. Values of $x_{methanol}$ calculated from Eq. (6) are plotted in Fig. 2.

4.3. Sintering model

The temperature-activated growth of metal particles on the catalyst support is known as metal sintering. This process reduces the metal surface area, thus decreasing catalytic activity throughout the bed. Following exposure of the sample to high temperatures, sintering occurs rapidly until the metal surface area reaches a new steady state level. The fractional rate of surface area loss with time [4] is given by the expression:

$$\frac{S}{S_0} = \frac{S_{steady\,state}}{S_0} + \left(1 - \frac{S_{steady\,state}}{S_0}\right)\exp(-k_s t) \qquad (7)$$

where S is the metal surface area of the sample and k_s a rate constant for metal sintering. The surface area of the sample prior to and at long times following exposure to high temperatures is indicated as S_0 and $S_{steady\,state}$, respectively. Assuming that the catalyst activity is proportional to the metal surface area, a time-dependent reaction rate constant can be written as

$$k = k_e \frac{SF_{methanol}}{S_0 W_{catalyst}P_{methanol}}(-2\ln(1 - x_{methanol}) - x_{methanol}) \qquad (8)$$

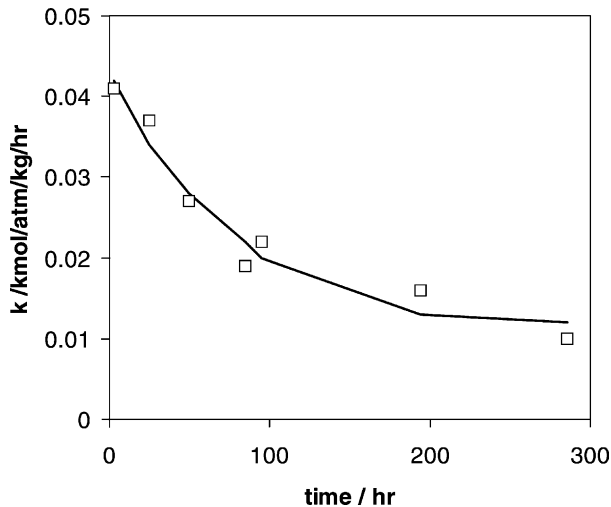where the ratio S/S_0 is calculated from Eq. (7).

Fig. 3. Deactivation by metal sintering. First order reaction rate constant, Eq. (5) vs. time for test #1. Solid line is calculated from Eq. (8) with parameters $k_e = 0.043$ mol/(atm kg h), $k_s = 0.013$ h^{-1}, and $S_{\text{steady state}}/S_0 = 0.253$.

5. Results

A total of five catalyst samples obtained from commercial manufacturers were tested for activity and durability as summarized in Table 1. In some tests, the conversion was measured both at the temperature of the test and at a lower temperature, usually 375 °C, to facilitate early detection of catalyst deactivation.

Methanol conversion versus time data showing a period of catalyst stability followed by rapid activity decay (deactivation by feed poisoning) were fitted using Eq. (6). Data showing rapid catalyst decay at short reaction times (deactivation

Table 3
Arrhenius parameters for fresh catalysts

Catalyst sample	Pre-exponential (mol/(s kg bar))	Activation energy (kJ/mol)
Sample A	7.8E+08	103
Sample C	9.3E+10	157
Sample B	4.8E+07	93
Sample D	8.5E+14	196
Sample E	5.2E+00	17
Reference [2]	1.4E+11	119

Table 4
Rate of catalyst deactivation by poisoning

Catalyst sample	T (°C)	Rate (g/1000 h)
Sample D, 1 atm, cycled	350	2.1
Sample D, 1 atm, cycled	400	3.3
Sample D, 1 atm, not cycled	400	0.7
Sample E, 1 atm, not cycled	400	1.9
Sample E, 1 atm, not cycled	450	1.8
Sample E, 1 atm, not cycled	500	1.9

by metal sintering) were fitted using Eq. (5) after substituting (8) and (7). Typical curve fitting results for poisoning and sintering are shown in Figs. 2 and 3, respectively. The adjustable parameters used to fit the experimental data were the initial value of the reaction rate constant, the rate of deactivation and, for those samples that deactivate by metal sintering, the asymptotic value for the fraction of initial surface area available for reaction, $S_{\text{steady state}}/S_0$.

Fig. 4 shows initial values for the reaction rate constant versus reciprocal temperature. Data for each individual catalyst give straight lines yielding the pre-exponential and activation energy values shown in Table 3. Reaction rate constants measured at atmospheric pressure vary between 0.1 and 1 mol/(atm kg h) for all catalysts at temperatures between 250 and 500 °C. While the activity levels are similar for all samples investigated, copper-based catalysts achieved
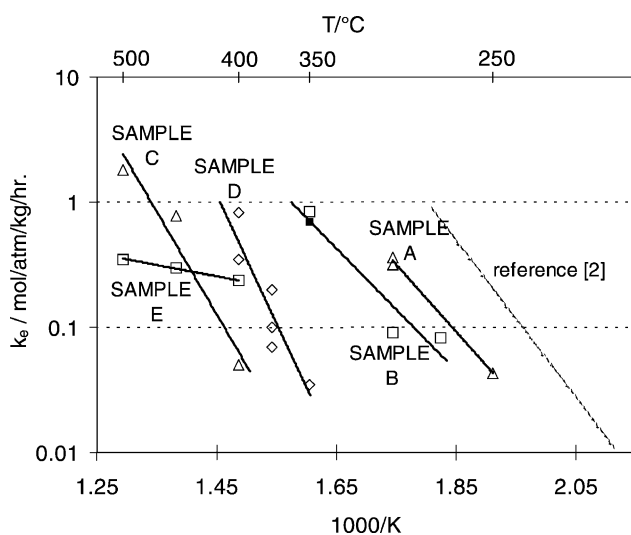

Fig. 4. First order reaction rate constant vs. reciprocal temperature for the catalyst samples indicated. Dashed line is from [2]. Results for copper-based catalysts (Samples A and B) were obtained at temperatures between 250 and 350 °C. Zinc, iron, and chromia preparations (Samples C, E, and D) were tested between 400 and 500 °C.
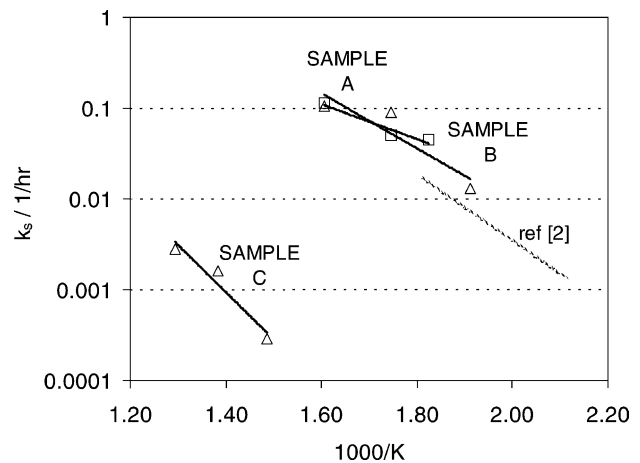

Fig. 5. Sintering rate constant vs. reciprocal temperature. Dashed line shows rate constants calculated from data in [2].

Table 5
Arrhenius parameters for deactivation by sintering

Catalyst sample	Pre-exponential (h^{-1})	Activation energy (kJ/mol)
Sample C	17,340	99
Sample B	130.1	37
Sample A	10,419	58

those levels at temperatures significantly lower than those needed by zinc, iron, or chromia preparations. The rate of catalyst degradation by feed poisoning is shown in Table 4 as mass of catalyst deactivated in 1000 h.

Fig. 5 shows an Arrhenius plot for the metal sintering rate constant. The straight lines in the figure yield the activation energies and pre-exponential factors presented in Table 5. Values of the deactivation rate constants for copper-based catalysts in Fig. 5 (Samples A and B) are larger than for a zinc-based catalyst (Sample C), indicating that copper preparations deactivate more rapidly than the zinc-based sample.

6. Discussion

Volume and weight restrictions on fuel processors require the use of highly active reforming catalysts capable of providing reaction rates higher than 0.5 mol/(s kg bar). The results presented above show that copper-based water-gas shift catalysts (Samples A and B) intended for service at approximately 200 °C deactivate rapidly when exposed to the high temperatures needed to obtain those high reaction rate levels. Iron and chromium-based preparations (Samples D and E) operate at even higher temperatures, but remain stable for thousands of hours.

Fig. 4 shows that copper-based catalysts Samples A and B can reach the high activity levels needed in fuel processors at temperatures between 300 and 350 °C, while zinc, iron, and chromium preparations require temperatures between 400 and 450 °C. Values for the Arrhenius parameters in Fig. 4 indicate that the activation energy for the effective first order reaction rate constant k_e is approximately the same for all catalysts investigated except for the iron preparation Sample E. Because the activation energy is related to the reaction mechanism (while the pre-exponential term is related to active metal dispersion), those similar values for the activation energy indicate that a rate controlling step, probably the water-gas shift reaction (2), is common to zinc, chromium, and copper catalysts. The much lower activation energy observed for the iron-based Sample E suggests that different reaction step, such as the methanol steam reforming reaction (1) might control the rate of reaction on iron catalysts.

Chromia supported iron and chromia supported zinc oxide catalysts (Samples E and D, respectively) deactivate following a feed poisoning model. Catalyst deactivation could be caused by an impurity that adsorbs strongly on the catalyst, or by physical loss of the active species. In either case, a sharp

front of deactivated catalyst moves down the reformer bed. This model contains two parameters, the reaction rate constant for fresh catalyst k_e, and the rate of deactivation k_{fp}. The rate constant can be calculated measuring the conversion of methanol at short reaction times, while the rate of deactivation is an adjustable parameter that should be a function of the feed flow rate. Because all tests but one were ran at the same flow rate, and in that one test two parameters were changed (flow rate and cycling), no correlation between flow rate and rate of deactivation can be inferred from the experimental results.

The results shown in Table 4 indicate that the operating temperature and thermal cycling have an impact on k_{fp}. The rate of deactivation increases with temperature, as expected if a reaction between a gas phase species and the solid catalyst deactivates the catalyst. Temperature cycling seems to have a strong detrimental effect on catalyst life: a sample exposed to temperature cycling between 400 °C and room temperature deactivated four times faster than a similar sample tested at a constant 400 °C. Whether temperature cycling enhances feed poisoning or other catalyst degradation mechanism remains to be understood.

Results obtained for zinc and copper catalysts were correlated using a metal sintering model. The mathematical form of this model is indistinguishable from expressions describing metal phase transitions and perhaps metal–support interactions; thus, we used the term metal sintering as a generic name that might include other temperature-activated processes. Model parameters are the initial rate of reaction k_e, the sintering rate constant k_s, and the ratio $S_{\text{steady state}}/S_0$. Fig. 5 suggests that the sintering rate constant obeys an Arrhenius law. This validates the model, since sintering is an activated rate process. Results for copper-based catalysts (Samples A and B, and [2]) can be correlated with a single straight line, indicating that the deactivation process is the same for all those catalysts. Values for k_s obtained for a zinc oxide preparation (Sample C in Fig. 5) are over an order of magnitude smaller than those observed on copper-based catalysts, suggesting that sintering processes are much slower for this zinc oxide-based catalyst. Values obtained for the ratio $S_{\text{steady state}}/S_0$ agree well with those presented in [2], indicating that our results are consistent with the results obtained by other authors.

7. Conclusions

Chromia supported iron and chromia supported zinc oxide (Samples D and E) commercialized for high temperature water-gas shift service exhibit acceptable activity and durability when used for methanol steam reforming. Copper/zinc oxide-based preparations deactivate rapidly when operated at the temperatures needed to obtain reaction rate levels similar to those observed for iron and chromium preparations. Iron-based catalyst Sample E is not desirable because it promotes the formation of methane. Kinetic modeling suggests that Sample D catalyst deactivates by feed poisoning. If the durability of this catalyst becomes an issue in fuel

processing applications, the mechanism of deactivation should be investigated further.

References

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