Journal of Catalysis **206,** 169–171 (2002)
doi:10.1006/jcat.2001.3465, available online at http://www.idealibrary.com on IDEAL®

RESEARCH NOTE

Are Noble Metal-Based Water–Gas Shift Catalysts Practical for Automotive Fuel Processing?

J. M. Zalc,* V. Sokolovskii,* and D. G. Löffler†,[1]

*Catalytica Energy Systems, Inc., 430 Ferguson Drive, Mountain View, California 94043; and †IdaTech, P.O. Box 5339, Bend, Oregon 97708

Received July 13, 2001; revised October 30, 2001; accepted October 30, 2001; published online January 14, 2002

Several Pt-based water–gas shift catalysts were prepared and tested for activity and stability. Under feed conditions typical of a reformer outlet, low activity and rapid first-order deactivation were observed. Virtually identical deactivation rates were found for all Pt/ceria water–gas shift catalysts tested. A strong dependence of the deactivation rate on the presence of hydrogen in the feed suggests that a large hydrogen fraction may lead to the irreversible overreduction of the ceria; this problem is likely to plague all such noble metal-based systems. © 2002 Elsevier Science (USA)

Key Words: **water–gas shift catalysts; carbon monoxide conversion; fuel processing; hydrogen production; PEM fuel cells.**

INTRODUCTION

Water–gas shift technology is well established for reducing CO levels in hydrogen streams used in large steady-state operations, such as hydrogen or ammonia plants. However, an automotive application poses an entirely different set of design challenges; a water–gas shift reactor for a fuel processor in such an environment must be cost-effective, lightweight, tolerant of road vibrations, and capable of rapid start-up (1, 2). All of these criteria must be met with a unit having a useful catalyst lifetime of $O(10^3)$ h while withstanding thousands of start-up and shutdown cycles.

In a fuel processor for a 50-kW automotive system, a steam or autothermal reformer would generate around 50–60 mol% hydrogen, accompanied by roughly 10% carbon monoxide, with the balance primarily composed of carbon dioxide, steam, nitrogen, and traces of unconverted fuel (3–5). The carbon monoxide level must be reduced to tens of ppm in order to avoid poisoning of current PEM fuel cells [6]. Efforts have been aimed at utilizing the water–gas shift (WGS) reaction (7, 8) ($CO + H_2O = CO_2 + H_2$) for primary CO cleanup and additional hydrogen generation, followed by a preferential oxidation step to reduce the CO level to about 10 ppm. The goal for a water–gas shift reactor is to reduce the CO level to not more than 1000 ppm to avoid hot spots in the preferential oxidation unit.

With the water–gas shift reaction, low temperatures result in low equilibrium levels of carbon monoxide although favorable kinetics occur at higher temperatures. To reach the low CO levels required at the inlet of the preferential oxidation unit, the outlet of the water–gas shift reactor must be at equilibrium at about 200°C. Thus, a suitable low-temperature WGS catalyst needs to have a high activity (at 200–300°C) and stability under a feed composition *typical of a reformer outlet*; yet, researchers (9, 10) have reported results for forward WGS rates on Pt/ceria formulations using feeds consisting of only steam, carbon monoxide, and diluent. Typically, the data have been collected over short time scales (a few hours). Reaction and deactivation kinetics were studied for a commercial iron oxide water–gas shift catalyst (11) but iron oxide catalysts are intended for high-temperature use, which is not suitable for achieving the carbon monoxide conversions needed in an automotive WGS reactor. Traditional commercial copper-based WGS catalysts require a lengthy *in situ* prereduction during which the temperature must be increased very gradually to prevent agglomeration of metal. This feature, along with the sensitivity of commercial Cu-based WGS catalysts to air and condensed water, has provided reason not to embrace them for an automotive fuel processing device, where air may leak into the catalyst chamber and moisture could condense on the catalyst upon shutdown. Consequently, there has been enthusiasm regarding the use of Pt-based WGS catalyst materials. We have developed several Pt-based WGS catalysts and tested them for activity and stability under realistic operating conditions in order to comment on their practicality for use in an automotive fuel processing application.

METHODS

Experiments were conducted in a conventional fixed-bed reactor situated inside a furnace. A catalyst bed containing

---

[1] To whom correspondence should be addressed. E-mail: dloffler@idatech.com.

catalyst particles ranging 0.42–0.50 mm in size and mixed with glass beads was located inside a pipe with inert glass bead sections upstream and downstream. The standard feed consisted of N_2, CO, CO_2, H_2, and H_2O. The gases (Scott Specialty Gases) were fed to the reactor by calibrated mass flow controllers, while a syringe pump was implemented to feed deionized water to an evaporator unit upstream of the reactor configuration. A backpressure regulator controlled the vessel pressure. For the results presented here, the catalyst was prepared by adsorption of diamminedinitritoplatinum(II) (Johnson Matthey) from nitric acid solution onto a ceria–zirconia based support. The catalyst was dried at 110°C overnight followed by calcination at 500°C for 4 h. The platinum loading determined by inductively coupled plasma analysis was 1.5 wt%. For all experimental conditions considered, diffusional resistances were negligible, as indicated by highly linear Arrhenius plots with initial activation energies around 70 kJ/mol. Effluent gases were analyzed via gas chromatography and during each run, the outlet carbon monoxide conversion was recorded as a function of time-on-stream.

The rate expression used for comparison of catalyst performance is given by Eq. [1]:

$$r_{\mathrm{wgs}} = k'(p_{\mathrm{CO}}\,p_{\mathrm{H_2O}} - p_{\mathrm{CO_2}}\,p_{\mathrm{H_2}}/K_{\mathrm{wgs}}). \qquad [1]$$

Here, r_{wgs} [=] (mol of CO/(g catalyst h)) is the local rate of reaction of carbon monoxide. It should be noted that this kinetic equation is not based on a mechanistic approach; rather it provides a reasonable model for comparing the performance of different catalysts. Equation [1], along with a first-order deactivation model that has a deactivation constant of k_{d} [=] h^{-1}, can be substituted into the isothermal, plug flow fixed-bed reactor design equation to obtain

$$\ln\left(\int_0^x \frac{dx}{(1-x)(\Theta_{\mathrm{H_2O}}-x)-K_{\mathrm{wgs}}^{-1}(\Theta_{\mathrm{CO_2}}+x)(\Theta_{\mathrm{H_2}}+x)}\right) = \ln\left(\frac{W}{F_{\mathrm{CO}}^0}\left(p_{\mathrm{CO}}^0\right)^2 k'\right) - k_{\mathrm{d}}t. \qquad [2]$$

Here, x is the conversion of carbon monoxide, K_{wgs} is the water–gas shift equilibrium constant, W is the mass of catalyst, F_{CO}^0 is the inlet molar flow rate of CO, p_{CO}^0 is the inlet partial pressure of CO, t is the time-on-stream, and each Θ_i is defined as p_i^0/p_{CO}^0. For brevity, let us denote the left-hand-side of Eq. [2] by α in the remainder of this document. For our standard operating conditions, the absolute pressure was 3 atm, $\Theta_{\mathrm{CO_2}} = 0.3$, $\Theta_{\mathrm{H_2}} = 1.5$, $\Theta_{\mathrm{H_2O}} = 3$, and $\Theta_{\mathrm{N_2}} = 1.5$. The catalyst space velocity was 2.5 (g catalyst h/mol of CO) in order to yield kinetic data for outlet conversions far from equilibrium. Values for α, k', and k_{d} were calculated from experiments conducted for catalyst bed temperatures of 250, 300, 350, and 400°C.

RESULTS AND DISCUSSION

Typical results for a 1.5% Pt/ceria system at 250°C are shown in Fig. 1. CO conversion falls rapidly during the first few hours to reach a constant rate of decay. Ignoring the first two data points, α values in the figure can be fit with a straight line. Based on the slope and intercept of the best-fit line, which had a correlation coefficient of 0.96, the initial activity and the deactivation coefficient were computed to be 0.25 (mol/($\mathrm{g_{cat}}$ h^{-1} atm^{-2})) and 0.009 h^{-1}, respectively.

In Ref. 10, Bunluesin *et al.* had investigated water–gas shift rates for ceria-supported noble metals using a feed consisting of CO, water, and N_2 under differential conditions. Rates were observed to be stable over several hours and diffusional limitations were absent. Based on their data, turnover frequencies can be estimated to be about 0.8 s^{-1} at 393°C, 0.2 s^{-1} at 300°C, and 0.04 s^{-1} at 200°C. The turnover frequencies computed for our Pt/ceria formulations were very similar to these values. It should be noted here that turnover frequencies far below 1 are considered to be too low for practical applications (12). Indeed, rough estimates of catalyst requirements based on initial activity reveal that approximately 50 kg of 1.5 wt% Pt catalyst would be needed for a 50-kW system. The reactor volume needed to contain such an amount of catalyst would be impractical in an automotive environment; the use of 750 g of platinum per reactor also raises serious cost issues.

In addition to exhibiting insufficient activity for transportation applications, Pt/ceria WGS catalysts deactivate rapidly. In fact, deactivation rates around 0.008 h^{-1} were observed for all the Pt-based WGS catalysts tested in our laboratory. In all cases, those deactivation rates were largely independent of temperature. A deactivation coefficient of

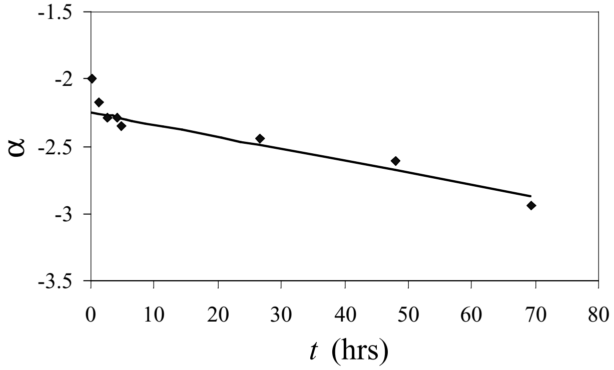

FIG. 1. A plot of α versus time-on-stream is shown for a 1.5% Pt/ceria catalyst. Correlation results reveal a deactivation coefficient of 0.009 h^{-1} and an initial activity of 0.25 (mol/($\mathrm{g_{cat}}$ h atm)) with a correlation coefficient of 0.95.

$0.008\ h^{-1}$ (using standard feed) corresponds to a catalyst half-life of around 100 h and indicates that an overdesign factor of about 500,000 in catalyst loading would be necessary to have 50% of the original activity after 2000 h on stream.

We concluded that the problem of deactivation is likely to be universal for all noble metal/ceria systems, probably because the presence of a significant fraction of hydrogen in the feed creates an environment that facilitates the irreversible overreduction of the support. In fact, significantly lower deactivation coefficients ($\approx 0.002\ h^{-1}$) were displayed when the hydrogen in the feed was replaced with nitrogen. Unfortunately, ceria must be present in the support because metal-support interactions are vital for catalyst function (13).

CONCLUSIONS

The activity of fresh Pt/ceria water-gas shift catalysts is not enough to meet the weight and cost constraints found in automotive applications. Furthermore, there is reason to believe that irreversible overreduction of the support leads to rapid deactivation of Pt/ceria water-gas shift catalyst systems operating under feed conditions typical of a reformer outlet. Deactivation rates observed translate into catalyst half-lives that are too short to be practical in an automotive application. Significantly lower deactivation rates were observed when hydrogen was not present in the feed. Attempts to rejuvenate the catalyst by heating under steam and under air were unsuccessful. This problem of deactivation is likely to plague all noble metal/ceria systems under such conditions but this effect has largely gone unnoticed because many researchers conducted experiments based on unrealistic feeds, excess catalyst, or short run lengths. Shifting efforts to the development and testing of stable, commercially viable, less expensive base-metal WGS catalysts should be a more fruitful endeavor.

ACKNOWLEDGMENTS

The authors thank Dr. Tae-Yun Park for his assistance in developing the experimental setup and for his insightful technical discussions. This work was supported by the Department of Energy, Office of Transportation Technologies.

REFERENCES

1. Ahmed, S., and Krumpelt, M., *Int. J. Hydrogen Energy* **26**, 291 (2001).
2. Rostrup-Nielsen, J. R., *Phys. Chem. Chem. Phys*. **3**, 283 (2001).
3. Brown, L., *Int. J. Hydrogen Energy* **26**, 381 (2001).
4. Basini, L., and Piovesan, L., *Ind. Eng. Chem. Res*. **37**, 258 (1998).
5. Doctor, A., and Lamm, A., *J. Power Sources* **84**, 194 (1999).
6. Larminie, J., and Dicks, A., "Fuel Cell Systems Explained." Wiley, New York, 2000.
7. Newsome, D., *Catal. Rev.–Sci. Eng*. **21**, 275 (1980).
8. Rhodes, C., Hutchings, G. J., and Ward, A. M., *Catal. Today* **23**, 43 (1995).
9. Li, Y., Fu, Q., and Flytzani-Stephanopoulos, M., *Appl. Catal. B* **27**, 179 (2000).
10. Bunluesin, T., Gorte, R. J., and Graham, G. W., *Appl. Catal. B* **15**, 107 (1988).
11. Keiski, R. L., Salmi, T., and Pohjola, V. J., *Acta Chem. Scand*. **44**, 777 (1990).
12. Boudart, M., and Djéga-Mariadassou, G., "Kinetics of Heterogeneous Catalytic Reactions." Princeton University Press, Princeton, New Jersey, 1984.
13. Trovarelli, A., *Catal. Rev*. **38**, 439 (1996).