

**Role of Metal-Support Interactions On The Activity Of Pt And Rh  
Catalysts For Reforming Methane And Butane<sup>†</sup>**

**Cecile Rossignol, Theodore Krause, and Michael Krumpelt**

Electrochemical Technology Program  
Chemical Technology Division  
Argonne National Laboratory  
9700 S. Cass Ave  
Argonne, IL 60439

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## **Role Of Metal-Support Interactions On The Activity Of Pt And Rh Catalysts For Reforming Methane And Butane**

Cecile Rossignol, Theodore Krause and Michael Krumpelt  
Argonne National Laboratory, 9700 South Cass Ave., Argonne, IL 60439

### Abstract

For residential fuel cell systems, reforming of natural gas is one option being considered for providing the H<sub>2</sub> necessary for the fuel cell to operate. Industrially, natural gas is reformed using Ni-based catalysts supported on an alumina substrate, which has been modified to inhibit coke formation. At Argonne National Laboratory, we have developed a new family of catalysts derived from solid oxide fuel cell technology for reforming hydrocarbon fuels to generate H<sub>2</sub>. These catalysts consist of a transition metal supported on an oxide-ion-conducting substrate, such as ceria, that has been doped with a small amount of a non-reducible element, such as gadolinium, samarium, or zirconium. Unlike alumina, the oxide-ion-conducting substrate has been shown to induce strong metal-support interactions. Metal-support interactions are known to play an important role in influencing the catalytic activity of many metals supported on oxide supports. Based on results from temperature-programmed reduction/oxidation and kinetic reaction studies, this paper discusses the role of the metal and the substrate in the metal-support interactions, and how these interactions influence the activity and the selectivity of the catalyst in reforming methane and butane to hydrogen for use in fuel cell power systems.

### Introduction

For residential fuel cell systems, reforming of natural gas is one option being considered to provide the H<sub>2</sub> required for the fuel cell to operate. Hydrogen can be produced from natural gas by partial oxidation, steam reforming, or pyrolysis. Industrially, most of the H<sub>2</sub> used in manufacturing processes, such as ammonia, is produced by steam reforming natural gas using a catalyst consisting of Ni supported on an alumina substrate, which has been modified to inhibit coke formation. Steam reforming is an endothermic reaction. The heat of reaction is provided by the combustion of methane using burners located external to the reforming reactor. Good control of the heat is required to provide a uniform temperature distribution throughout the steam reformer.

Autothermal reforming is an alternative approach for reforming methane that can be viewed as a combination of partial oxidation and steam reforming. In autothermal reforming, both oxygen (generally supplied as air) and steam are fed along with methane into the reactor. The ratio of oxygen to carbon (O<sub>2</sub>:C) is maintained at about 0.5, so that the overall heat of reaction (oxidation plus steam reforming) is close to zero. Because the heat required for the steam reforming reactions is generated within the reactor, an autothermal reformer can respond more rapidly, with better temperature control, to changing power demands than a steam reformer. For this reason, autothermal reforming has received considerable attention for the on-board generation of H<sub>2</sub> in fuel cell powered vehicles. The reaction of methane with oxygen can occur either with or without a catalyst. In the absence of a catalyst, the reaction occurs in the gas-phase (termed a homogeneous reaction). Temperatures of >1000°C are required to achieve high reaction rates. In the presence of a catalyst, the reaction occurs at the catalyst surface (termed a heterogeneous reaction). In a catalytic process, high reaction rates can be achieved at much lower temperatures (<600°C). These lower reaction temperatures provide a number of advantages, including (1) a simpler reactor design requiring less thermal integration, (2) a wider choice of materials of construction, and (3) a reduced potential for coking.

At Argonne National Laboratory, we are developing new catalysts for autothermal reforming [1]. Our catalysts are derived from solid oxide fuel cell materials, where a transition metal is supported on an oxide-ion-conducting substrate, such as ceria, zirconia, or lanthanum gallate that has been doped with a small amount of a non-reducible element, such as gadolinium or samarium. Ceria-based materials are being investigated as potential catalysts for CO and hydrocarbon oxidation reactions because of the redox and oxygen storage/release properties of ceria [2]. The catalytic activity of ceria can be further enhanced by the addition of dopants, in particular, such as Gd<sup>3+</sup> or Sm<sup>3+</sup>, which have been shown to increase the number of oxygen vacancies, improve the oxygen mobility and oxygen ion conductivity, and enhance the redox and

oxygen storage/release properties of ceria. The role of defects and surface oxygen vacancies in determining the catalytic behavior of these metal/mixed oxide systems is well known [3,4]. The role of the transition metals is less well understood. Transition metals, in particular noble metals, not only catalyze many oxidation reactions, including the combustion of hydrocarbons, but also enhance the redox properties of ceria. In this paper, we discuss how both the metal and the dopant affect the catalytic properties of these ceria-based catalysts, and how these properties relate to the catalysts' autothermal reforming activity.

## Experimental

Gadolinium-doped ceria samples, with Gd doping ranging from 0-0.2 mol percent, were made by coprecipitation of the nitrate salts of Ce and Gd. For brevity, the nomenclature CGO-X is used, where X refers to the mole fraction of Gd in the doped ceria; e.g.,  $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.90}$  is referred to as CGO-20. Nitrate salts of Pt or Rh were loaded onto the oxide support using the incipient wetness technique, generally at a weight loading of 0.5 wt%. Platinum (5 wt%) and Rh (0.5 wt%) supported on  $\gamma\text{-Al}_2\text{O}_3$  were purchased from Aldrich. Temperature-programmed reaction experiments (heating rate of  $2^\circ\text{C}/\text{min}$ ) were performed on powder samples ( $\sim 50$  mg) using a Zeton Altamira AMT-100 Chemisorption unit equipped with a quadrupole mass spectrometer and a thermal conductivity detector. The catalyst samples were not reduced prior to the reaction experiments. All experiments were conducted using a reactant gas mixture which consisted of either methane or isobutane at flowrates ranging from 0.3 to 1.0 mL/min, along with  $\text{O}_2$  at various flowrates such that the  $\text{O}_2:\text{C}$  ratio was below the stoichiometric ratio required for complete combustion, with the balance He for a total reactant flowrate of  $\sim 50$  mL/min.

## Results and Discussion

The temperature-programmed reactions of  $\text{O}_2 + \text{CH}_4$  and  $\text{O}_2 + \text{C}_4\text{H}_{10}$ , both under fuel-rich conditions ( $\text{O}_2:\text{C}$  ratio of 0.4), were studied to investigate the affect of the support (either  $\text{Al}_2\text{O}_3$  or CGO-20) on the catalytic activity of Pt and Rh.

Figures 1 and 2 compare the light-off temperatures for the oxidation of methane and isobutane under fuel-rich conditions respectively, catalyzed by Pt-CGO-20, Pt- $\text{Al}_2\text{O}_3$ , Rh-CGO-20, and Rh- $\text{Al}_2\text{O}_3$ . Several general observations can be made from these results. First, the light-off temperature for isobutane is significantly lower than the light-off temperature for methane when catalyzed by Pt-CGO-20, Pt- $\text{Al}_2\text{O}_3$ , and Rh- $\text{Al}_2\text{O}_3$ , but slightly higher when catalyzed by Rh-CGO-20. Second, the light-off temperature for either isobutane or methane at a given  $\text{O}_2:\text{C}$  ratio is always lower for Pt- $\text{Al}_2\text{O}_3$  than for Rh- $\text{Al}_2\text{O}_3$ . There is little difference in the light-off temperature of methane at a given  $\text{O}_2:\text{C}$  ratio catalyzed by Pt-CGO-20 or Rh-CGO-20. Third, the light-off temperature for both methane and isobutane decreases as the  $\text{O}_2:\text{C}$  ratio decreases for all four catalysts.

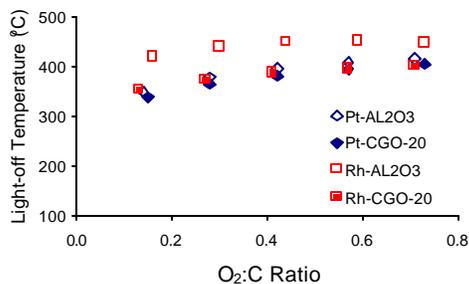


Figure 1. Light-off temperature for methane oxidation as a function of  $\text{O}_2:\text{C}$  ratio for Pt- $\text{Al}_2\text{O}_3$ , Pt-CGO-20, Rh- $\text{Al}_2\text{O}_3$ , and Rh-CGO-20.

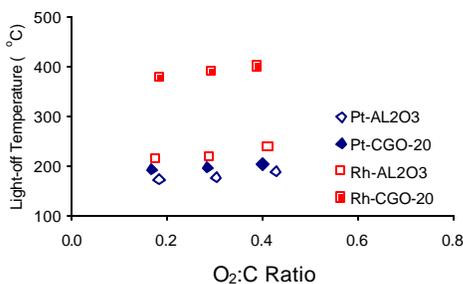


Figure 2. Light-off temperature for isobutene oxidation as a function of  $\text{O}_2:\text{C}$  ratio for Pt- $\text{Al}_2\text{O}_3$ , Pt-CGO-20, Rh- $\text{Al}_2\text{O}_3$ , and Rh-CGO-20.

Figures 3 and 4 show the product yield ( $H_2$ ,  $H_2O$ ,  $CO$ , and  $CO_2$ ,) and unreacted  $CH_4$  and  $O_2$  for the temperature-programmed reaction of  $O_2 + CH_4$  under fuel-rich conditions ( $O_2:C = 0.4$ ) catalyzed by Pt-CGO-20 and Rh-CGO-20, respectively. Light-off occurs at about the same temperature for Pt-CGO-20 ( $383^\circ C$ ) and Rh-CGO-20 ( $388^\circ C$ ) despite the fact that differences are observed in the interaction of the two metals with  $O_2$  below the light-off temperature. For Rh-CGO-20,  $O_2$  uptake begins at  $\sim 300^\circ C$  with essentially complete uptake of  $O_2$  occurring before light-off. For Pt-CGO-20,  $O_2$  uptake begins at a higher temperature ( $\sim 350^\circ C$ ) with as much as 50% of the initial  $O_2$  still present in the product gas just before light-off occurs ( $383^\circ C$ ). The only products observed are  $CO_2$  and  $H_2O$  below the light-off temperature. After light-off, methane reacts with  $H_2O$  and possibly  $CO_2$  to generate  $CO$  and  $H_2$ . With CGO-20 (no Pt or Rh), light off was not observed over the temperature range investigated.

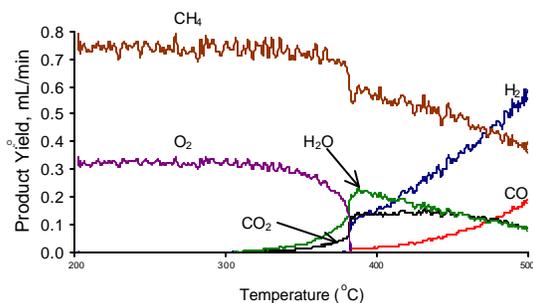


Figure 3. Product yield for temperature-programmed reaction of  $O_2+CH_4$  ( $O_2:C=0.4$ ) for Pt-CGO-20.

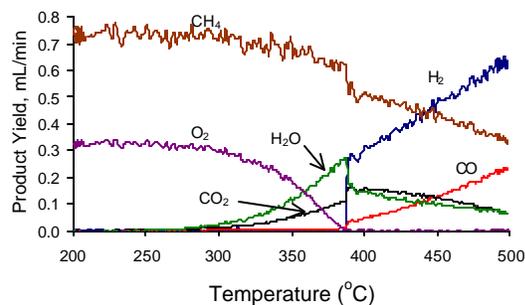


Figure 4. Product yield for temperature-programmed reaction of  $O_2+CH_4$  ( $O_2:C=0.4$ ) for Rh-CGO-20.

Figures 5 and 6 show the product yield ( $H_2$ ,  $H_2O$ ,  $CO$ ,  $CO_2$ , and  $CH_4$ ) and unreacted  $C_4H_{10}$  and  $O_2$  for the temperature-programmed reaction of  $O_2 + C_4H_{10}$  under fuel-rich conditions ( $O_2:C = 0.4$ ) catalyzed by Pt-CGO-20 and Rh-CGO-20, respectively. Unlike methane where the temperature dependent product yields for Pt-CGO-20 and Rh-CGO-20 are similar (Figs. 3 and 4), distinct differences are observed in the temperature dependent product yield for isobutane for the two different catalysts. The most notable difference is that the light-off temperature of isobutane for Pt-CGO-20 ( $204^\circ C$ ) is almost  $200^\circ C$  lower than for Rh-CGO-20 ( $401^\circ C$ ). The large decrease in the light-off temperature of isobutane compared to methane for Pt-CGO-20 is similar to that observed for Pt- $Al_2O_3$  and Rh- $Al_2O_3$  (Figs. 1 and 2). As before,  $CO_2$  and  $H_2O$  are the only reaction products observed during light-off. For Pt-CGO-20, steam and/or  $CO_2$  reforming does not occur below  $400^\circ C$  and complete conversion of  $C_4H_{10}$  is observed at  $>650^\circ C$ . For Rh-CGO-20, the light-off temperature of isobutane ( $401^\circ C$ ) is slightly higher than the light-off temperature of methane ( $388^\circ C$ ); however, once light-off occurs, steam and/or  $CO_2$  reforming occur quite rapidly, with complete isobutane conversion observed at  $<650^\circ C$ .

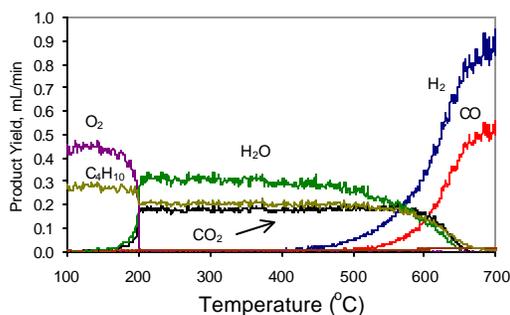


Figure 5. Product yield for temperature-programmed reaction of  $O_2+C_4H_{10}$  ( $O_2:C=0.4$ ) for Pt-CGO-20.

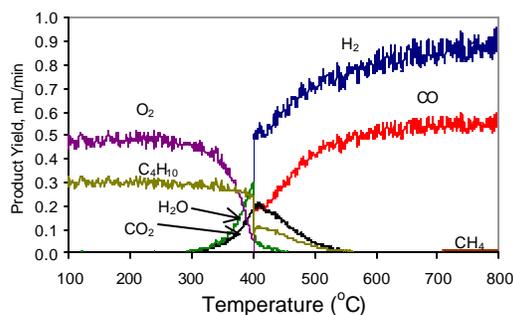


Figure 6. Product yield for temperature-programmed reaction of  $O_2+C_4H_{10}$  ( $O_2:C=0.4$ ) for Rh-CGO-20.

Veser et al [5] studied the oxidation of C<sub>1</sub>-C<sub>4</sub> alkanes on noble metal-foil catalysts (Pt, Pd, Rh, and Ir). They observed that (1) the light-off temperature decreases as the hydrocarbon chain length increases which was attributed to the decrease in the C-H bond strength with increasing chain length, (2) the light-off temperature decreases as the O<sub>2</sub>:C ratio decreases, which was attributed to competitive adsorption between the hydrocarbon and oxygen (because of the higher sticking coefficient of oxygen, lower O<sub>2</sub>:C ratios favor the adsorption of the hydrocarbon), and (3) the light-off temperature increases as the metal-oxygen bond strength increases (Pt<Pd<Rh<Ir). In our study, the results from the oxidation of methane and isobutane catalyzed by Pt-Al<sub>2</sub>O<sub>3</sub> or Rh-Al<sub>2</sub>O<sub>3</sub> are consistent with the observations of Veser et al. Our results suggest that the interaction between Pt or Rh and the alumina support may be minimal under the reaction conditions. In contrast, the results from the oxidation of methane and isobutane catalyzed by Pt-CGO-20 or Rh-CGO-20 cannot be completely explained by the observations of Veser et al. The small difference in the light-off temperature of methane between Pt-CGO-20 and Rh-CGO-20 at a given O<sub>2</sub>:C ratio suggests that factors other than the relative strength of the metal-oxygen bond may be important. For Rh-CGO-20, the fact that the light-off temperature for isobutane is slightly higher than the light-off temperature for methane (compared to the other three catalysts in this study where a significant decrease was observed in the light-off temperature for isobutane compared to methane) suggests that C-H bond activation may not be involved in the rate limiting step for the oxidation reaction on Rh-CGO-20. These results suggest that the CGO-20 substrate influences the catalytic activity of Pt and Rh, although the nature of this interaction is not fully understood. Further studies are in progress to better elucidate the interaction between Rh or Pt and CGO-20.

### Conclusions

The four catalysts studied, Pt-Al<sub>2</sub>O<sub>3</sub>, Pt-CGO-20, Rh-Al<sub>2</sub>O<sub>3</sub>, and Rh-CGO-20, catalyze the oxidation of methane and isobutane under fuel-rich conditions. For Pt-Al<sub>2</sub>O<sub>3</sub> and Rh-Al<sub>2</sub>O<sub>3</sub>, the general trends observed in this study, i.e., the light-off temperature of isobutane is lower than that of methane for a given catalyst and the light-off temperatures observed for methane and isobutane for Pt are lower than for Rh, agree well with the trends reported by Veser et al for the oxidation of alkanes catalyzed by noble-metal foils. This suggests that the interaction between Pt and Rh the alumina support may be minimal under these reaction conditions. For Rh-CGO-20, the fact that the light-off temperature of isobutane is slightly higher than the light-off temperature of methane and that this catalyst is more active for steam and/or CO<sub>2</sub> reforming at lower temperatures than Pt-CGO-20 suggests that there is a strong interaction between Rh and the CGO support. Work is in progress to characterize the nature of this interaction.

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