

Argonne National Laboratory Reforming Work

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Objectives

- Develop reforming catalyst for diesel fuel.

Key Milestones

- Defined approach for developing more durable diesel reforming catalysts

Approach

In FY 2003, Argonne continued its work in bipolar plate materials development and began work in two new areas that are critical for the SECA program: chromium volatility and diesel reforming. Bipolar plate materials and chromium volatility are discussed in another abstract elsewhere in this report.

Converting diesel fuel into a hydrogen-rich gas for solid oxide fuel cells is important for the development of auxiliary power units for heavy duty vehicles. Presently known catalysts supporting the auto-thermal reforming reaction degrade rapidly. Sulfur poisoning is one issue, but loss of noble metal by evaporation is a more serious one. Our approach to solving the durability issue will be to develop binary oxides that do not contain noble metals. Currently, only catalysts containing platinum offer enough tolerance to sulfur, but the platinum

consolidates and evaporates in a few hundred hours. We have evidence that certain binary oxides can accelerate the autothermal reforming reaction, and we anticipate reasonable activities and stabilities.

Results

This report represents the start-up of the research activity in the diesel reforming program. We have carried out our effort in several research areas concurrently. These efforts include a) modification of a micro-reactor test plant for diesel catalyst evaluation, b) synthesis of new reforming catalysts, and c) evaluation of new diesel reforming catalysts under various reforming conditions.

Shown in Figure 1 is the micro-reactor test plant modified for diesel catalyst evaluation.

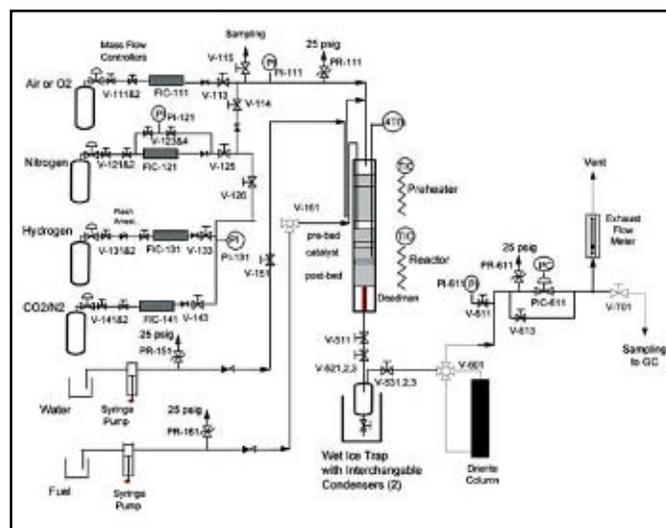


Figure 1. Schematic drawing of the micro-reactor for the diesel reforming study.

The center of the system is a plug-flow reactor, which is constructed with thin-wall stainless steel tubing. Inside of the reactor is divided into two sections, preheater and reactor, respectively.

The reactants for the fuel input mixture are provided through several parallel supply lines outside of the reactor, according to Figure 1. For example, we use high purity dry air from the storage tank through a carefully calibrated mass flow controller (FIC-111). The

water and fuel are supplied through separate lines by the metered syringe pumps. Additional gas supply lines are also available to add the flexibility for alternative input mixture preparation. For example, CO₂/N₂ can be added to study reforming using recycled SOFC effluent stream. Depending on the catalyst load, we can control the input gas hourly space velocity from 20,000 to over 200,000 hr⁻¹ under normal operating conditions.

The reformatte effluent from the catalytic reaction is analyzed through the gas chromatography (GC). The moisture in the sample is first reduced by an ice trap followed by a Drierite column. This arrangement allows us to probe not only the key reformatte components (H₂, CO, CO₂, CH₄, N₂) but also light residual hydrocarbons (C₂H₄, C₂H₆, C₃H₆, C₃H₈, etc.) with high accuracy, but without the interference of the steam. Therefore, all the product concentrations reported in our study are dry percentage based. In addition, heavier hydrocarbon fractions formed through reforming, with boiling point above ~0 °C will also be trapped in the ice condenser. Although we routinely observe hydrocarbon condensate during the reforming experiment, its portion is relatively low, especially under the reforming condition where the input fuel conversion is relatively high.

The surrogate fuel used for the initial phase of the study is high purity dodecane obtained directly

from Aldrich Chemicals. Dodecane was chosen for the initial investigation because its molecule formula represents closely to the average hydrocarbon composition in the diesel. Other surrogate fuels are also planned in our future study in understanding the impact of different diesel components toward the reforming efficiency and coke formation.

The first group of perovskite catalysts investigated were substituted on the “B” site. The catalysts were made by combustion synthesis, and then calcined in dry air for 1 hour at temperatures of 800 °C, 1000 °C and 1200 °C. They were also heated at 1200 °C in hydrogen for 24 hours. The specific surface area of all the catalyst samples were characterized through a nitrogen adsorption (BET) method using Micrometrics ASAP 2000, after out-gassing the samples in vacuum at 120 °C. Listed in Table 1 are the results obtained through this study.

All the powder calcined at 1200 °C, under air or H₂, show a very low surface area (~3m²/g). The surface area increases when the temperature of calcination decreases. The PV calcined at 1200°C and milled 7 days have a higher surface area than those that have not been milled.

Most of the samples listed in Table 1 were first screened for catalytic activity through a fast reactor before being subjected to full-scale test plant study. The

Composition	Treatment	SA (m ² /g)
PV	1200	2.7
	1000	5.4
	800	10.6
	1200 H2	2.8
	1200 pwdr milled 7D	7.7
PV-ns	1200	3.6
	1000	
	800	12.0
	1200 H2	
PV-A	1200	3.1
PV-B	1200	2.4

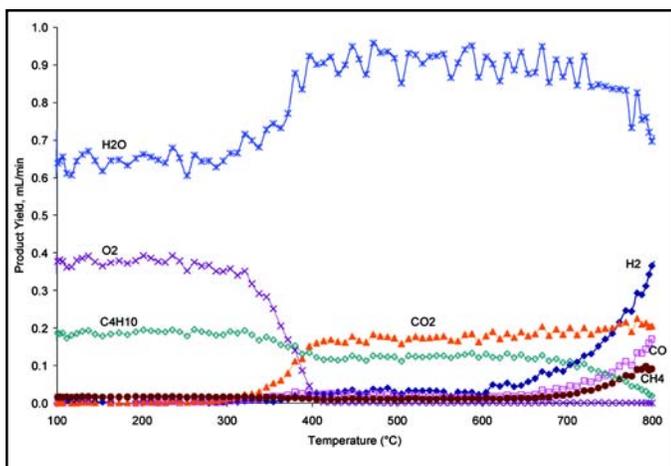


Figure 2. Reformate product yield for sample PV calcined at 1200 °C.

screening was conducted by fast microreactor (Altamira Zelton) under ATR reforming condition. Isobutane was used as the test fuel and input mixture was adjusted so that O_2/C ratio is equal to 0.5 and H_2O/C ratio is 0.85. For each test, 50 mg of powder was used. The ramp rate is 5 °C/min and the total flow is 50 ml/min.

Figure 2 shows key reformate component yields as a function of reaction temperature during ATR reforming of isobutene over PV_1200 without the dopant (PV calcined at 1200 °C). The H_2 yield appears at temperatures above 600 °C and does not reach the maximum at 800 °C. All samples treated under different temperatures showed similar behavior. The difference in calcination temperatures and the surface area does not seem to have much impact on the catalytic activity.

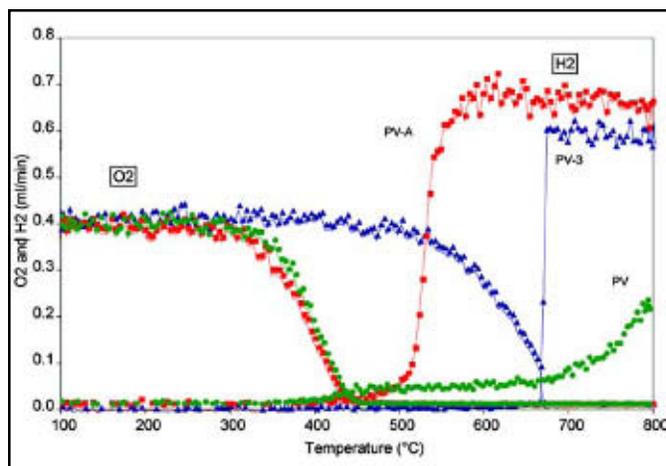


Figure 3. Comparison of O_2 and H_2 concentrations over PV, PV-A and PV-B during reforming of isobutene.

The catalytic activity, however, demonstrates remarkable difference when the catalysts were modified on the B site. Figure 3 shows the O_2 consumption and H_2 yield during ATR reforming of isobutene over the catalyst PV-A and PV-B as the function of temperature in comparison with PV_1200. Clearly, PV-A and PV-B demonstrated a better catalytic activity than that of PV-1200, with the hydrogen production light-off temperature at 530 °C and 675 °C, respectively. These temperatures are significantly lower than that by PV-1200, which does not reach the full light-off even at 800 °C. There is a difference in the light-off curves between PV-A and PV-B. In PV-A, H_2 concentration does not increase instantaneously at the exhaust of O_2 . In PV-B, it does. This observation suggests that the oxidation of hydrogen is more facile than that of carbon monoxide over PV-A surface. This order is reversed in the case of PV-B.

Conclusions

It appears that novel catalysts supporting the autothermal reforming of diesel fuel surrogates can be found. Future work will address the space velocities and cost, and will also involve durability issues with surrogate and actual diesel fuels.