# Supported Rh Catalysts for the Indirect Partial Oxidation of Isooctane

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**Abstract**−The production of hydrogen from isooctane over three rhodium-based catalysts has been examined. The reaction entailed total oxidation of a proportion of the fuel followed by reforming of isooctane to produce hydrogen. Rhodium (1% wt) was impregnated on three different supports: alumina, ceria-alumina, and ceria-zirconia. No differences in catalytic activity were observed, but reaction yield changed with the support. Ceria-zirconia was found to be the preferred support since methanation did not occur over the catalyst.

Key words: Gasoline, Isooctane, Partial Oxidation, Sol-gel, TPO

## INTRODUCTION

The control of vehicle exhaust emissions using catalytic converters is well established [Lox and Engler, 1997]. However, increasingly stringent legislation has led to consideration of alternative means of reducing emissions, with the fuel cell powered vehicles being considered in some depth [Trimm and Önsan, 2001]. The optimum unit for vehicle applications has been found to be the polymer electrolyte membrane fuel cell (PEMFC), but the cells have the disadvantage that they operate only on hydrogen as a fuel. Since the distribution of hydrogen is difficult and storage of hydrogen in a vehicle adds weight, consideration has been given to the conversion of more readily available fuels to hydrogen on board the vehicle.

Such conversion can be achieved by autothermal steam reforming, in which part of the fuel is oxidised to produce heat and part is steam reformed to produce hydrogen [Ma, 1995]

$$CH_4+O_2=CO_2+2H_2O$$
$$CH_4+H_2O=CO+3H_2$$
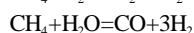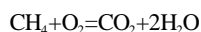
or by partial oxidation [Pena et al., 1996]

$$CH_4+1/2O_2=CO+2H_2$$
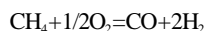
The partial oxidation of several fuels has been examined, ranging from methanol [Zum Mallen and Schmidt, 1996] to petrol [Jenkins and Shutt, 1989]. The autothermal reforming of methane [Ma, 1995], methanol [Ma et al., 1996] and light hydrocarbons [Ma, 1995] has also been reported. The present study deals with the conversion of isooctane, used as a model for gasoline, to hydrogen

$$C_8H_{18}+25/2O_2=8CO_2+9H_2O \tag{1}$$

$$C_8H_{18}+4O_2=8CO+9H_2 \tag{2}$$

$$C_8H_{18}+8H_2O=8CO+17H_2 \tag{3}$$

$$CO+H_2O=CO_2+H_2 \tag{4}$$

The investigation has been focused on the conversion of octane under oxygen deficient conditions pertinent to partial oxidation [reac-

tion (2)]. Rhodium, an active catalyst for partial oxidation and steam reforming [Burke, 2001], was deposited on three different supports and used to catalyse the reactions.

## EXPERIMENTAL

Three rhodium-based catalysts, namely $Rh/Al_2O_3$, $Rh/CeO_2$-$ZrO_2$, and $Rh/CeO_2/\delta Al_2O_3$, were used in all experiments. $Al_2O_3$ and $CeO_2$-$ZrO_2$ supports were prepared by sol-gel [Praharso et al., 2001], and $CeO_2/\delta$-$Al_2O_3$ support was prepared by sequential impregnation method. The $\delta$-$Al_2O_3$ was obtained from $\gamma$-$Al_2O_3$ by thermally treating the latter at $1,000\,°C$. This ensures that possible phase changes under reaction conditions are minimised. Rhodium (1% wt) was deposited onto three supports by impregnation techniques. All precursors were calcined in air at $600\,°C$ for 4 hours. Prior to use, the resulting catalysts were reduced *in-situ* by using a mixture of 5% hydrogen in nitrogen.

A conventional fixed bed flow reactor system was used to undertake all experiments. The bed contained 0.2 g of catalysts diluted in 1.8 g of $\alpha$-$Al_2O_3$ packed in two wads of quartz wool. Isooctane was picked up by argon via a water-bathed saturator controlled at $20\,°C$ and subsequently diluted by argon to obtain a feed composition of 1% on mole basis. A total flow rate of 200 mL min$^{-1}$ STP was maintained by the use of Brooks mass flow controllers. A carbon to oxygen ratio of 1:1.56 was employed. The reaction temperature was monitored by a thermocouple inserted in the catalyst bed. The disappearance of reactants and the appearance of products were examined (by the use of a mass spectrograph) as a function of temperature, using a transient-steady state control sequence. Temperature was ramped at $5\,°C$ min$^{-1}$ from ambient to $600\,°C$.

## RESULTS AND DISCUSSION

The conversion of liquid fuels to hydrogen is usually initiated at temperatures greater than room temperature. This is achieved by combusting part of the fuel [Trimm and Önsan, 2001]. It is necessary to establish the temperature at which combustion becomes significant (light off temperature), and the first objective was to determine this value for isooctane. As seen from Fig. 1, the value ob-

Comparsion of reactant distribution for partox of iso-octane [C/O ratio 1:1.56]
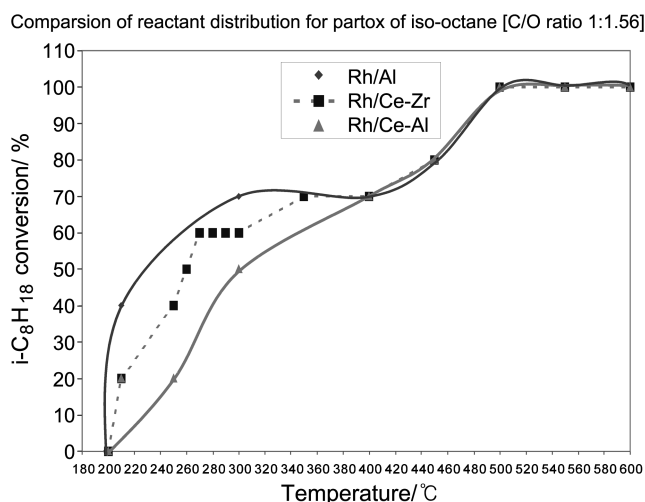


Fig. 1. Support effect towards partox of isooctane.

Reactant/product distribution for partox of iso-octane
Rh/CeO$_2$-ZrO$_2$ cat. Total flow 200 mL/min. Inlet i-octane 1%, C/O ratio 1:1.56
Reduced catalyst



Fig. 2. H$_2$ formation and O$_2$ consumption at lower temperature.

served was independent of the support used with oxidation becoming important above 200-220 °C.

Inspection of the results allowed the identification of two distinct reaction regimes. The initial heat release was very high, tending to stabilise at about 60% conversion. However above ca. 300 °C, conversion increased again at a slower rate until complete conversion was observed at about 500 °C. Some explanation of these results was obtained by measuring oxygen consumption and hydrogen production (cf. Fig. 2). Oxygen was consumed at low temperatures and was totally removed by 300 °C. Hydrogen production was observed starting at about 275 °C but becoming significant only after complete depletion of oxygen. This would suggest that hydrogen production results from reforming rather than from partial oxidation

$$C_8H_{18}+8H_2O=8CO+17H_2 \tag{3}$$

$$C_8H_{18}+8CO_2=16CO+9H_2 \tag{5}$$

$$CO+H_2O=CO_2+H_2 \tag{4}$$

with the H$_2$O and CO$_2$ arising from Eq. (1).

In agreement with this, the experimental values of the H$_2$/CO ratio were found to lie in the range 1.8-1.9, which is close to the ratio of 2.1 predicted from Eq. (3) and very different from a ratio of 1.1 predicted from Eq. (2). Thus, it would seem that hydrogen is produced by a combination of total oxidation and reforming, rather than by partial oxidation.

The product spectrum showed some interesting trends at higher temperatures. Above ca. 450 °C, methane was observed over some catalysts and distinct changes were observed in the carbon monox-
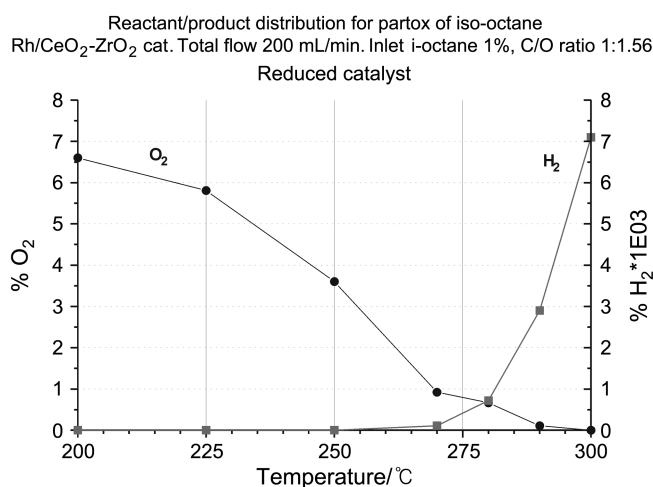
ide/carbon dioxide ratio. The hydrogen yield at 400, 500, and 600 °C, defined as the amount observed as a percentage of that expected on the basis of the thermodynamics of reaction (2) was also found to vary with the nature of the support. Results are summarised in Table 1.

From Table 1, it is evident that for all three catalysts, the stoichiometric ratio, CO/CO$_2$, increases with temperature indicating that CO$_2$ produced during total oxidation was later consumed, most likely via CO$_2$ dry reforming of the remaining isooctane. Although ceria is a good WGS catalyst, since the CO/CO$_2$ ratio in WGS is 1, this reaction would not be responsible for the trend observed. However, the influence of ceria (which has high adsorption capacity for H$_2$O) is evident in the H$_2$/CO ratio. The two catalysts containing ceria displayed a higher H$_2$/CO ratio at all temperatures, suggesting greater steam reforming activity. Even so, this activity drops with temperature due to the contribution of CO from dry reforming. Indeed, both steam and dry reforming appeared to contribute evenly to the overall H$_2$ and CO production especially at 600 °C. Stoichiometrically, the H$_2$/CO ratio from steam reforming is about 2.1, while that from dry reforming is about 0.6. It would seem that as temperature increased, dry reforming gained prominence. However, the presence of ceria seemed to give greater weight to steam reforming. Consistent with this, when ceria was absent (as in the Rh/Al$_2$O$_3$ catalyst) dry reforming contributed more significantly to overall H$_2$/CO as may be evident from a value of 1 seen for this catalyst.

Interestingly, CH$_4$ was produced only at 500 °C and on Rh/Al and Rh/Ce-Al indicating that the ZrO$_2$ support does not enhance methanation. This is probably due to the fact that alumina support shows better hydrogenation activity than zirconia as previously ob-

**Table 1. Products of reaction**

| Catalyst | Rh/Al$_2$O$_3$ | | | | Rh/CeO$_2$-$\delta$ Al$_2$O$_3$ | | | | Rh/CeO$_2$-ZrO$_2$ | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Temperature, °C | 400 | 450 | 500 | 600 | 400 | 450 | 500 | 600 | 400 | 450 | 500 | 600 |
| H$_2$/CO | 1.0 | 1.4 | 1.7 | 1.2 | 3.7 | 2.8 | 1.8 | 1.4 | 2.6 | 2.2 | 1.9 | 1.4 |
| CO/CO$_2$ | 0.4 | 0.6 | 0.4 | 1.5 | 0.2 | 0.3 | 0.4 | 1.4 | 0.1 | 0.3 | 0.6 | 1.3 |
| CH$_4$/CO$_2$ | 0 | 0.06 | 0.4 | 0 | 0 | 0.04 | 0.4 | 0 | 0 | 0 | 0 | 0 |
| H$_2$ yield, % | 42 | - | 88 | 100 | 77 | - | 90 | 100 | 40 | - | 100 | 100 |

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Product distribution for partox of iso-octane, 0.2 g of Rh/Al₂O₃ cat.
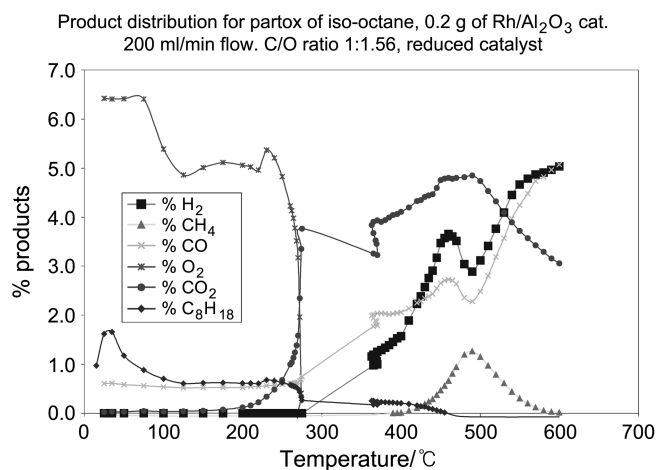200 ml/min flow. C/O ratio 1:1.56, reduced catalyst



**Fig. 3. Product distribution for partox of iso-octane (Rh/Al₂O₃ catalyst). Inlet isooctane: 1%, Ar as diluent: 187.5 ml min⁻¹, temperature-ramp: 5 °C min⁻¹, H₂O product was not shown.**

served [Chen and Adesina, 1994; Anderson, 1984]. The product distribution data (Table 1) indeed show the appearance of $CH_4$ in the product stream over Rh/Al and Rh/Ce-Al from about 450 °C which then disappeared at 600 °C probably due to steam reforming. This explanation is further supported by transient mass spectrometer data (cf. Fig. 3) which show a peak in $CH_4$ production precisely at the minima of $H_2$ and CO curves, i.e., $CH_4$ arises from the $CO-H_2$ reaction.

## CONCLUSIONS

This study has compared the activities of Rh catalysts on three different supports for partial oxidation of isooctane. It was found that under sub-stoichiometric conditions the total oxidation could be obtained exclusively followed by in-situ usage of the $CO_2$ and $H_2O$ to carry out dry and steam reforming of the oxidised isooctane. The product distribution was then a function of both catalyst support and temperature.

## ACKNOWLEDGEMENTS

## REFERENCES

Anderson, R. B., "Fischer-Tropsch Synthesis," Academic Press, Orlando, Fl. (1984).

Burke, N. R., "Control of Vehicle Cold-start Emissions," PhD Thesis, University of New South Wales, Sydney, Australia (2001).

Chen, H. and Adesina, A. A., "Semiconductor Oxide Supports for Fischer-Tropsch Synthesis Catalysts: Selectivity and Activity Studies," Proceedings 44th Canadian Society for Chemical Engineering Conference, Calgary, Canada, Oct. 2-5 (1994).

Ma, L., Jiang, C., Adesina, A. A., Trimm, D. L. and Wainwright, M. S., "Simulation Studies of Autothermal Reactor System for $H_2$ Production from Methanol Steam Reforming," *The Chem. Eng. Journal*, **62**, 103 (1996).

Jenkins, J. W. and Shutt, E., "The Hot Spot Reactor," *Plat. Metals. Rev.*, **33**, 118 (1989).

Lox, E. S. J. and Engler, B. H., in "Handbook of Heterogeneous Catalysis," G. Ertl, H. Knözinger and J. Weitkamp (eds.), Weinheim, Germany, VCH. 4, 1559 (1997).

Ma, L., "Hydrogen Production from Steam Reforming of Light Hydrocarbons in an Autothermic System," PhD Thesis, University of New South Wales, Sydney, Australia (1995).

Pena, M. A., Gomez, J. P. and Fierro, J. L. G., "New Catalytic Routes for Syngas and Hydrogen Production," *App. Catal. A: General*, **144**, 7 (1996).

Praharso, Adesina, A. A., Trimm, D. L. and Cant, N. W., "Unpublished Results" (2001).

Trimm, D. L. and Önsan, Z. I., "Onboard Fuel Conversion for Hydrogen-fuel-cell-driven Vehicle," *Catal. Rev. Sci. Eng.*, **43**, 31 (2001).

Zum Mallen, M. P. and Schmidt, L. D., "Oxidation of Methanol over Polycrystalline Rh and Pt: Rates, OH Desorption, and Model," *J. Catal.*, **161**, 230 (1996).