

Supported Rh Catalysts for the Indirect Partial Oxidation of Isooctane

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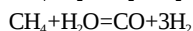
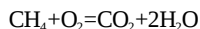
Abstract—The production of hydrogen from isooctane over three rhodium-based catalysts has been examined. The reaction entailed total oxidation of a proportion of the fuel followed by reforming of isooctane to produce hydrogen. Rhodium (1% wt) was impregnated on three different supports: alumina, ceria-alumina, 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

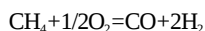
INTRODUCTION

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]



or by partial oxidation [Pena et al., 1996]



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



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/Al₂O₃, Rh/CeO₂-ZrO₂, and Rh/CeO₂/δ-Al₂O₃, were used in all experiments. Al₂O₃ and CeO₂-ZrO₂ supports were prepared by sol-gel [Praharso et al., 2001], and CeO₂/δ-Al₂O₃ support was prepared by sequential impregnation method. The δ-Al₂O₃ was obtained from γ-Al₂O₃ 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 α-Al₂O₃ 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-

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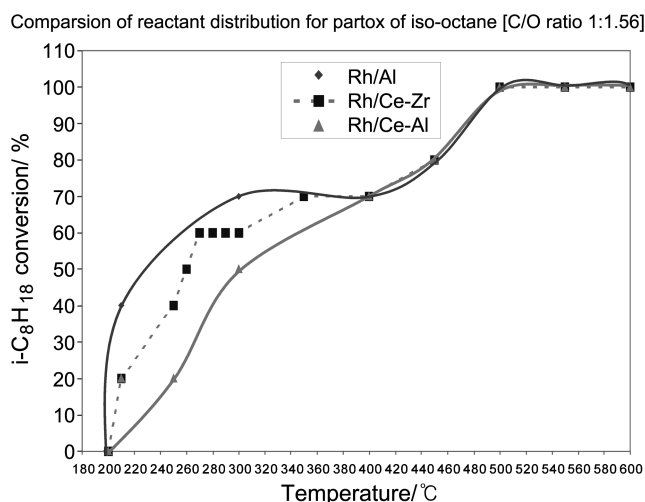


Fig. 1. Support effect towards partox of isooctane.

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



with the H_2O 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-

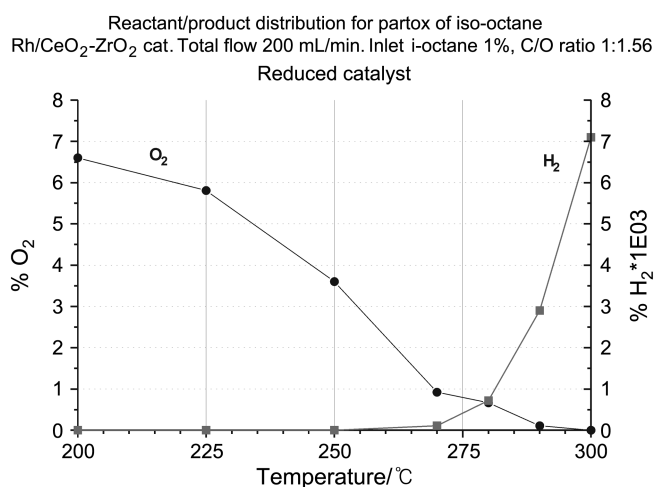


Fig. 2. H_2 formation and O_2 consumption at lower temperature.

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_2O) 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 $\text{Rh}/\text{Al}_2\text{O}_3$ 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 $\text{Rh}/\text{Ce-Al}$ 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_2O_3				Rh/ CeO_2 - δ Al_2O_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

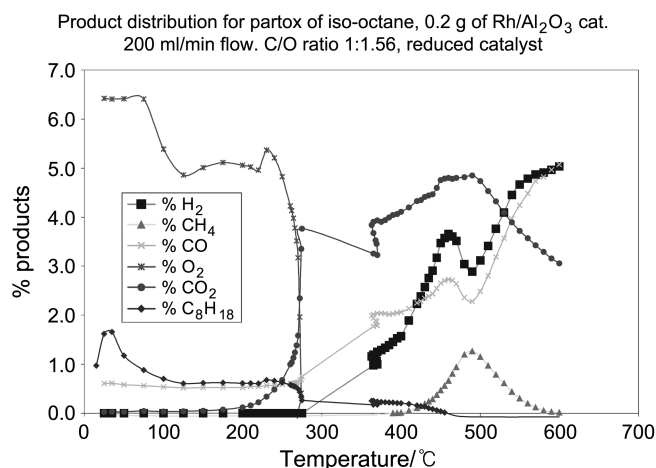


Fig. 3. Product distribution for partox of iso-octane (Rh/Al₂O₃ catalyst). Inlet iso-octane: 1%, Ar as diluent: 187.5 ml min⁻¹, temperature-ramp: 5 °C min⁻¹, H₂O product was not shown.

served [Chen and Adesina, 1994; Anderson, 1984]. The product distribution data (Table 1) indeed show the appearance of CH₄ 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 CH₄ production precisely at the minima of H₂ and CO curves, i.e., CH₄ arises from the CO-H₂ reaction.

CONCLUSIONS

This study has compared the activities of Rh catalysts on three different supports for partial oxidation of iso-octane. It was found that under sub-stoichiometric conditions the total oxidation could be obtained exclusively followed by in-situ usage of the CO₂ and H₂O to carry out dry and steam reforming of the oxidised iso-octane. The product distribution was then a function of both catalyst support and temperature.

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