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# Steam reforming of *n*-butane on Pd/ceria

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We have examined the steam reforming of *n*-butane on ceria, 1 wt% Pd/ceria, 1 wt% Pd/alumina, and 15 wt% Ni/silica between 573 and 873 K, with $H_2O:C$ ratios between 1.0 and 2.0. No stable rates could be observed on Ni/silica due to rapid coking under these conditions. While rates were stable on the other catalysts, Pd/ceria showed a much higher activity than either Pd/alumina or ceria individually. Of additional interest, $CO_2:CO$ ratios were much higher on Pd/ceria and approached equilibrium. The reaction order for *n*-butane on Pd/ceria was 0.15. For $H_2O$, reaction order changed from 0.6 to zero at the stoichiometric, *n*-butane : $H_2O$ ratio. It is suggested that the high activity of Pd/ceria for this reaction is due to a dual-function mechanism, in which ceria can be oxidized by $H_2O$ and then supply oxygen to the Pd.

**KEY WORDS:** *n*-butane; steam-reforming; ceria; Pd/ceria; Pd/alumina; Ni/silica; fuel cells

## 1. Introduction

Steam reforming of light hydrocarbons is important for the production of $H_2$ and synthesis gas. Methane is obviously the most important hydrocarbon used for the production of $H_2$ [1]; however, higher hydrocarbons may also be reformed. Commercial catalysts are generally based on Ni, e.g., $Ni/Al_2O_3$ or Ni/MgO [1], and coke formation is a significant problem, especially when higher hydrocarbons ($C_2$ and larger) are reformed with low $H_2O:C$ ratios [1–5]. Research on the development of coke-resistant catalysts has focused primarily on modification of supported Ni. For example, the addition of small amounts of $SnO_2$ [6,7], $MoO_3$ [8–12], and $WO_3$ [12] and the use of different supports [6,7] has been shown to increase the resistance of Ni catalysts to coking.

With the need for on-board reforming for fuel-cell applications, there has been renewed interest in more active and selective catalysts for reactions like steam reforming, water–gas shift, and $CO_2$ reforming. The requirements for this application are quite different from that used for chemical production, since "on-board" reformers should be compact and heat integration for the system may not be as efficient. The development of more active catalysts that can operate under more severe conditions and lower $H_2O:C$ ratios could have significant advantages. While the cost of the catalysts used in these special-application reformers is still important, the different constraints imposed by the new applications suggest that one can take a renewed look at precious-metal catalysts.

In general, precious metals do not exhibit as high a propensity as Ni to form coke, so that one might expect precious-metal catalysts to be able to function under more severe conditions. Furthermore, while the literature for steam reforming on precious-metal catalysts is limited, there is evidence that these materials can be active catalysts [1,13]. However, it should be noted that there are discrepancies in the literature. For example, data quoted in [1] for steam reforming of $CH_4$ suggests that turnover frequencies for Pd/silica are very similar to those found for Ni/MgO, while measurements in our own laboratory indicated that rates on 10% Pd/silica were at least hundred times lower than rates on 10% Ni/alumina [14,15].

It has been shown that ceria-supported Pd and Ni catalysts are much more active for steam reforming of $CH_4$ than similar catalysts prepared on non-reducible supports [14,15]. For example, the steam-reforming rates for Pd/ceria were higher than that for Pd/silica by a factor of $10^4$. This has been explained by invoking a dual-function mechanism, in which $CeO_2$ transfers oxygen to the supported metal and is, in turn, re-oxidized by $H_2O$. The mechanism is shown below, with $\sigma$ representing sites on the precious metal:

$$CH_4 + \sigma \rightleftharpoons CH_{x,\mathrm{ads}} + (4-x)H_{\mathrm{ads}} \tag{1}$$

$$H_2O + Ce_2O_3 \rightleftharpoons 2CeO_2 + H_2 \tag{2}$$

$$2H_{\mathrm{ad}} \rightleftharpoons H_2 + \sigma \tag{3}$$

$$CH_{x,\mathrm{ads}} + 2CeO_2 \rightleftharpoons CO_x + (x/2)H_2 + Ce_2O_3 + \sigma \tag{4}$$

The key feature in this mechanism is that oxygen from $CeO_2$ can react with species on the metal, as shown in reaction (4). Reaction (4) probably occurs by first transferring oxygen to the Pd, where coadsorbed $O_{\mathrm{ad}}$ and $CH_{x,\mathrm{ad}}$ react to products. There is a great deal of evidence that oxygen transfer from $CeO_2$ to Pd occurs. For example, TPD studies of CO from various metals deposited onto ceria supports show that a significant fraction of the CO desorbs as $CO_2$ [16]. Most recently, Smirnov and Graham have provided spectroscopic data showing that Pd films deposited onto a ceria–zirconia substrate are oxidized when heated in vacuum [17].

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Finally, similar redox mechanisms involving oxygen transfer from $CeO_2$ to a metal can be used to explain the high rates and observed kinetics for CO oxidation [18,19], the water–gas-shift reaction [20], and $CO_2$ reforming of $CH_4$ on ceria-supported metals [21]. Of additional interest for the present study, Pd/ceria catalysts appeared to be extremely stable towards coke formation, both in the harsh environments found for $CO_2$ reforming and with steam reforming of $CH_4$ at low $H_2O:CH_4$ ratios.

Because Pd/ceria catalysts are so active and stable for $CH_4$ reforming, we set out to examine the activity and stability of this catalyst for $n$-butane reforming. We will demonstrate that Pd/ceria is indeed a very active catalyst for this reaction, showing significantly higher rates than that found for ceria, Pd/alumina, or Ni/silica under the same conditions. Moreover, Pd/ceria shows excellent stability, even down to $H_2O:C$ ratios approaching unity.

## 2. Experimental

The ceria used in this work was formed by thermal decomposition of $Ce(NO_3)_3{\cdot}6H_2O$ (Alfa Aesar, 99.5%), as reported in a previous publication [21,22], and was found to have a surface area of 30 $m^2/g$ [22]. The alumina ($\gamma$-$Al_2O_3$ (Alfa Aesar, 96%)) and silica (North America Silica Company) were used as received. Catalytic metals were added by incipient wetness using aqueous solutions of $Pd(NH_3)_4(NO_3)_2$ or $Ni(NO_3)_2$. The Pd/alumina and Pd/ceria catalysts were loaded to a level of 1 wt% Pd, while the Ni/silica was loaded to 15 wt% Ni. After addition of the metal salts, the catalysts were dried and then calcined at 873 K for approximately 6 h in air.

Rate measurements were performed in a tubular, fixed-bed reactor, 0.6 mm in diameter, between 470 and 800 K. The total pressure was fixed at 1 atm; but the partial pressures of the reactants were varied by changing the relative flow rates of $n$-butane, He, and a He–$H_2O$ mixture. The amounts of catalyst used for the rate measurements were between 30 and 50 mg and the total flow rate of gas to the reactor was maintained at approximately 120 ml/min. The reactants and products were analyzed with an on-line GC, (model SRI8610C) equipped with a TCD detector and using a Hayesep D column. For all measurements where rates are reported, the conversion of the limiting reagent was kept below 10%, so that differential conditions could be assumed. For calculation of the limiting reagent, the stoichiometric reaction was assumed to be $C_4H_{10} + 8H_2O \rightleftharpoons 4CO_2 + 13H_2$. Also, the reaction was allowed to run for at least 30 min prior to each data point, so that the rates may be considered to have stabilized.

## 3. Results

Figure 1 shows the rate of $n$-butane conversion as a function of temperature for 11.5 Torr $n$-butane and 92 Torr $H_2O$ over Pd/ceria, Pd/alumina, and ceria. Rates are not shown for the Ni/silica catalyst because stable rates could not be obtained between 620 and 820 K, where products were observed for these partial pressures. Indeed, at the onset of reaction on Ni/silica, we observed consumption of $n$-butane, but with no products leaving the reactor, demonstrating that there was severe coking on this catalyst. (Steam reforming of carbon in the absence of a catalyst was negligible under our conditions.) In contrast to Ni/silica, the other catalysts were quite stable. Pd/ceria was the most active of these catalysts, with rates about six times higher than that of Pd/alumina. The activation energies for these two catalysts were also approximately the same at 60 kJ/mol. Ceria by itself showed some activity, which is probably not surprising given that it is a reasonably good oxidation catalyst [23]. However, the rates on Pd/ceria are clearly higher than the sum of the rates on Pd/alumina and ceria, so that interactions between Pd and ceria must contribute to the high activity of the Pd/ceria catalyst.

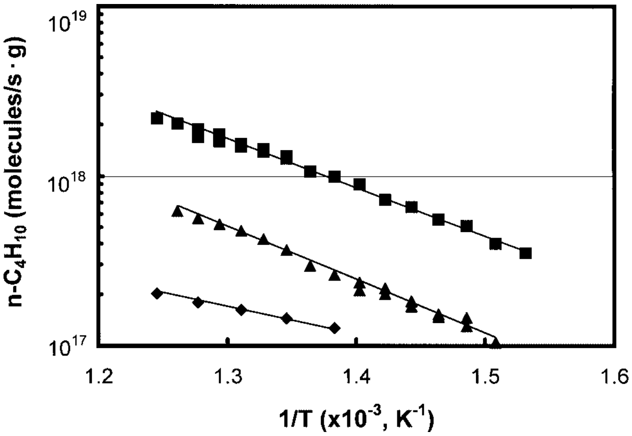

Figure 1. Arrhenius plots for steam reforming of $n$-butane over $CeO_2$ (♦), $Pd/CeO_2$ (■), and Pd/$\gamma$-$Al_2O_3$ (▲). Data were collected with 11.5 Torr $n$-butane and 92 Torr $H_2O$.

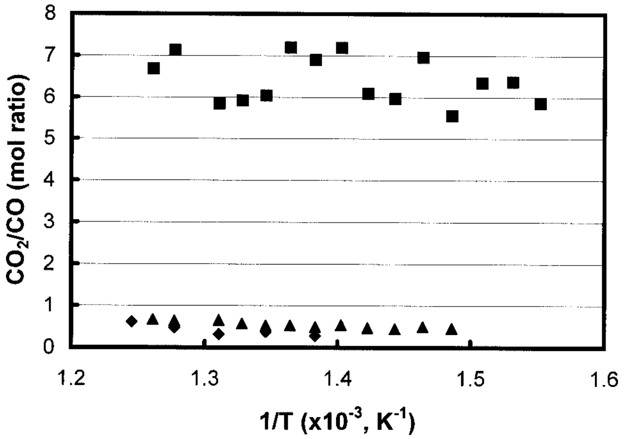

Figure 2. $CO_2/CO$ ratios corresponding to the steam-reforming data in figure 1. The data is shown for $CeO_2$ (♦), $Pd/CeO_2$ (■), and Pd/$\gamma$-$Al_2O_3$ (▲).

Of additional interest, the primary carbon-containing product for the Pd/ceria catalyst was $CO_2$, even under these differential reactor conditions with the relatively low $H_2O:C$ ratio of 2 in the reactants. This is shown in fig-

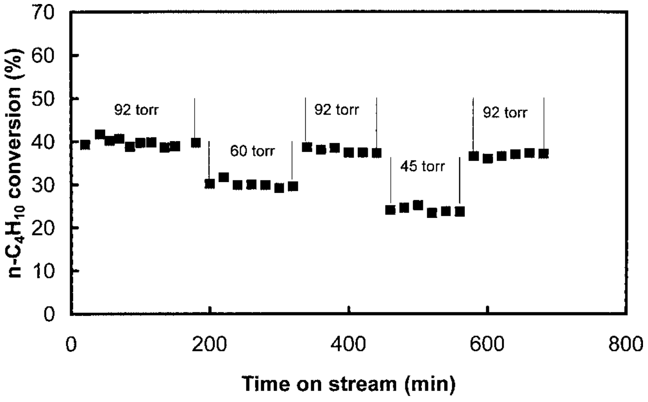

Figure 3. The conversion as a function of time for steam reforming of *n*-butane over Pd/$CeO_2$. Data were collected at 773 K with 11.5 Torr *n*-butane and $H_2O$ pressures as shown.

ure 2, along with similar data for Pd/alumina and ceria. The equilibrium ratios for $CO_2 : CO$ under our conditions were greater than 20 in all experiments, so that equilibrium did not limit reaction. On Pd/alumina and ceria, the ratio was less than unity, while the ratio ranged between 6 and 7 on Pd/ceria. Since Pd/ceria is a very good water–gas-shift catalyst [20,24], one can probably consider the formation of $CO_2$ to be the result of a sequential reaction; however, taken together with the high rates found on this catalyst, the formation of $CO_2$ is an additional bonus, since it reduces the load on the water–gas-shift reactor. Finally, we did not observe any hydrocarbon products, such as methane, a minor product observed in earlier studies on zirconia-supported Rh and Ru [13].

We next examined the stability of the Pd/ceria catalyst at 773 K, using 150 mg of catalyst with a total flow rate of 120 ml/min and a partial pressure of 11.5 Torr *n*-butane, as shown in figure 3. The conversion remained quite stable at 40% for a period of 200 min at 92 Torr $H_2O$, a $H_2O : C$ ratio of 2.0. For comparison, the equilibrium conversion of *n*-butane, assuming $CO_2$ as the product, is ~60% under these conditions. Also, we measured the $CO_2 : CO$ ratio to be approximately 4, essentially equal to the equilibrium value. When the $H_2O$ pressure was lowered to 60 Torr ($H_2O : C$ ratio of 1.5), the conversion dropped to 30% but remained stable. Furthermore, the conversion essentially returned to its original value when the $H_2O$ pressure was again increased to 92 Torr after 120 min. We obtained reasonably steady conversions for 120 min at 45 Torr $H_2O$ ($H_2O : C$ ratio of 1.0), although the conversion was slightly reduced when we increased the $H_2O$ pressure back to 92 Torr. This may suggest that there is some deactivation of the catalyst at the very low $H_2O : C$ ratios. Heating the catalyst in air restored the catalyst to its initial activity.

Finally, we examined the partial pressure dependences, as shown in figure 4 at 723 K. In figure 4(a), the *n*-butane conversion is plotted as a function of *n*-butane partial pressure, holding the $H_2O$ pressure at 92 Torr. We observed only a moderate increase in the rate of *n*-butane conversion in going from 3 Torr *n*-butane to 18 Torr *n*-butane, so that the calculated reaction order was 0.15. In figure 4(b), rates are shown as a function of $H_2O$ pressure, holding the *n*-butane pressure at 11.5 Torr. Since 92 Torr of $H_2O$ would correspond to the stoichiometric reactant ratio, there seems to be a change in the reaction order for $H_2O$, depending on which reactant is rate limiting. In excess $H_2O$, the reaction rate was essentially independent of $H_2O$ pressure, while the reaction order was approximately 0.6 at lower $H_2O$ pressures. It is noteworthy that the reaction order was ~0.5 for $H_2O$ in the water–gas-shift reaction as well [20], which might be expected if reoxidation of the $Ce_2O_3$ (reaction (2) in the mechanistic scheme shown in section 2) were rate limiting.

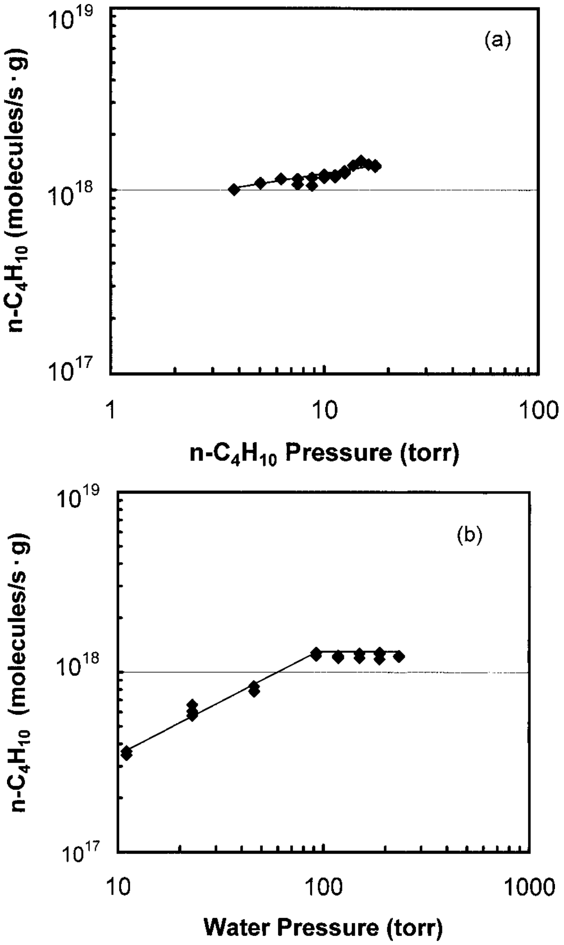

Figure 4. Partial pressure dependences for steam reforming of *n*-butane over Pd/ceria at 723 K. (a) Differential rates as a function of *n*-butane partial pressure with a $H_2O$ partial pressure of 92 Torr. (b) Differential rates as a function of $H_2O$ partial pressure with an *n*-butane partial pressure of 11.5 Torr.

## 4. Discussion

The data shown in this paper demonstrate that Pd/ceria is a very good catalyst for *n*-butane reforming. We observed stable rates at $H_2O : C$ ratios as low as 1.0 at 773 K, while we were unable to even measure rates on a Ni/silica catalyst at a $H_2O : C$ ratio of 2.0 at these temperatures. As an added bonus, the primary product of the reforming reaction on Pd/ceria is $CO_2$, even at low conversions. The fact that rates on Pd/ceria were much higher than on either Pd/alumina or ceria by itself lends support to mechanistic concepts discussed in section 1, where oxygen transfer from $CeO_2$ to the precious metal is an important step on ceria-supported catalysts. Furthermore, the activation energy and the $CO_2$-production rates for steam reforming of methane [14], performed on essentially identical catalysts to those examined in the present study, were very similar to the rates observed here for $n$-butane reforming. Since $n$-butane should dissociate much more readily than methane on Pd, it appears that the rates on Pd/ceria may be limited by the rate of oxygen transfer. Based on this mechanism, one should expect Pt/ceria and Rh/ceria to show similar activities.

One would obviously prefer to work with less expensive metal catalysts, such as Ni, Co, or Fe, or with inexpensive metal oxides [1]. In the case of Ni, it is known that ceria can also enhance the steam reforming properties [15,25], and it appears that the mechanistic concepts discussed here for the precious metals also apply to Ni/ceria catalysts [24]. However, Ni, Co, and Fe all tend to catalyze formation of graphite fibers [26,27], so that coking will almost certainly be unavoidable at low $H_2O:C$ ratios. While some metal oxides show activity for steam reforming [28], the activities tend to be low. Clearly, one needs to examine catalytic materials that can activate C–H bonds without catalyzing graphite formation and Pt, Pd, and Rh would appear to have the ideal properties for this.

Only a relatively small number of studies have been reported in the literature for steam reforming of higher hydrocarbons using precious metals. Of these, work by Igarashi et al. on steam reforming of $n$-butane on Rh/zirconia is quite significant [13]. Not only do they report stable rates for $H_2O:C$ ratios of 1.0, but they also reported high $CO_2:CO$ ratios in their products. We suggest that their results are due to a similar redox mechanism to that discussed here. Even though zirconia is not normally thought of as a reducible oxide, a recent study from our group has shown that zirconia can undergo reduction and oxidation [21], possibly associated with the surface [29]. These redox properties of zirconia appear to be responsible for the high catalytic activity found for $CO_2$ reforming of $CH_4$ by Pd/zirconia [30].

Oxy-reforming, the reforming of hydrocarbons in the presence of steam and $O_2$, has been examined on alumina-supported precious metals; and it has been demonstrated that Pd/alumina is an excellent catalyst for these reactions [31]. From a mechanistic standpoint, the oxy-reforming and steam-reforming reactions are virtually identical. One can obviously oxidize Pd directly from the gas phase in oxy-reforming, but oxygen transfer from $CeO_2$ to Pd has been demonstrated [17]. In both reactions, the catalyst is exposed to a net reducing environment, so that one should not expect major differences in the oxidation states of the catalyst. Given the high activity of Pd/ceria for catalytic oxidation, water–gas shift, and steam reforming, it is not surprising that these materials show superior performance in this role.

The cost of precious-metal-containing catalysts may also not be prohibitive. The materials we examined in this study were not optimized and we did not try to determine the performance at lower metal loadings. Even so, the metal loadings in our catalysts were much lower than one usually sees in more traditional, Ni-based catalysts. Furthermore, we did not examine mixed-oxide supports, like ceria–zirconia, which is known to provide better oxygen transfer than pure ceria [23]. Therefore, significant improvements can almost certainly be made in the catalytic performance of these materials. We believe ceria-supported, precious metals may well find application for steam reforming of hydrocarbons under some conditions.

## 5. Conclusions

We have demonstrated that Pd/ceria is an active and stable catalyst for steam reforming of $n$-butane. Under conditions that caused immediate coking on Ni/silica, the reaction rates on Pd/ceria were stable. The reaction occurs through a dual-function mechanism, in which the hydrocarbon is activated on the Pd and then oxidized by $CeO_2$. Finally, the primary C-containing product from the reaction on Pd/ceria is $CO_2$.

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