Kinetic studies of methane steam reforming on ceria-supported Pd

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Steady-state, steam-reforming rates for methane were measured on model and high-surface-area, ceria-supported Pd catalysts and compared to rates on Pd/silica between 600 and 825 K. Specific rates on Pd/ceria were higher than those on Pd/silica by a factor of 10^5 and were higher even than rates reported in the literature for Ni catalysts. Model catalysts prepared with Pt or Rh on ceria also showed very high rates, essentially identical to rates for Pd/ceria. However, catalysts prepared by addition of Pd to ceria which had been calcined to high temperatures (>1175 K) before the addition of Pd were not active. Based on these results, we suggest that steam reforming on ceria-supported catalysts occurs through a bifunctional mechanism in which oxygen from ceria reacts with dissociated methane on the precious metal. High-temperature calcination of ceria significantly changes its reducibility, so that the reaction is not enhanced.

Keywords: water–gas shift, CO oxidation, oxygen storage, ceria-supported catalysts, Pt, Pd, Rh

1. Introduction

Ceria is widely used in automotive, emissions-control catalysis as an oxygen-storage component, giving up oxygen under reducing conditions and taking up oxygen under oxidizing conditions. Because oxygen desorption from ceria occurs at very high temperatures [1], oxygen-storage requires contact between ceria and a precious metal, with the reduction of ceria occurring through reaction with a reductant on the precious metal [2,3]. This reaction between ceria and molecules adsorbed on supported, precious metals has been observed in both transient and steady-state reaction measurements [3–10]. For example, in the case of both the CO oxidation and the water–gas-shift reaction, a second rate process has been observed which gives significant rate enhancements over that found on either precious metals or ceria individually [9,10].

Interactions between ceria and precious metals are especially important in the water–gas-shift reaction, where rates can be higher than those on the individual components by several orders of magnitude [10]. A mechanism which explains the high activity of ceria-supported metals is as follows:

$$CO + \sigma \rightarrow CO_{ad} \qquad (1)$$

$$H_2O + Ce_2O_3 \rightarrow 2CeO_2 + H_2 \qquad (2)$$

$$CO_{ad} + 2CeO_2 \rightarrow CO_2 + Ce_2O_3 + \sigma \qquad (3)$$

Here, σ represents a site on the precious metal. This mechanism is supported by additional evidence. First, the rates are found to be zeroth-order in CO, as expected for reducing conditions in which the precious metals are saturated with CO. Second, rates on ceria-supported Pt, Pd, and Rh are identical, so that reaction appears to be limited primarily by the transfer of oxygen from ceria [11]. Finally, high-temperature calcination of the ceria, which is known to significantly decrease its reducibility, significantly decreases the observed rates and eliminates this bifunctional process. Based on the above mechanism, one should expect significant enhancements for the rates of other reactions involving oxidation by water over precious metals. In particular, we were interested in steam reforming of methane and other hydrocarbons, both for automotive catalysis (the reactions not only eliminate hydrocarbons but produce H_2, which is an effective reductant for NO [2]) and for fuel cells [12]. Because precious metals and ceria individually exhibit very low activities for steam reforming, the kinetics of this reaction may also be informative in regards to the oxygen-storage properties of the oxide.

In the present paper, we will show that ceria-supported Pd does indeed exhibit excellent rates for steam reforming of methane, showing higher activities than Ni/silica in the low-temperature range we investigated. As with the water–gas-shift reaction, high-temperature calcination of ceria, prior to the addition of Pd, decreased the reaction rates significantly, by several orders of magnitude in this case.

2. Experimental

Two different types of ceria-supported catalysts were used in this study. The first sets of experiments were performed on the same model catalysts used in earlier studies of CO-oxidation and water–gas-shift kinetics [9,10]. For these, ceria films, $\sim 10\ \mu$m in thickness, were synthesized by spray pyrolysis with a 0.1 M, aqueous solution of $Ce(NO_3)_3$ onto nonporous α-alumina plates, held at ~ 575 K. The films were then calcined at various temperatures between 575 and 1670 K for 1 h in air prior to vapor deposition of the precious metal. Vapor deposition ensured that the precious metals were present only at the external surfaces of the film. Also, because the ceria films were calcined prior to addition of the catalytic metals, deactivation of the ceria could be accomplished without changing the dispersion of the catalytic metal. The second set of catalysts was prepared by wet impregnation of porous ceria (prepared by calcination of $Ce(NO_3)_3\cdot 6H_2O$ at 973 K) and silica (Ultrasil-VN3-SP, Degussa) supports using aqueous solutions of $Pd(NH_4)_4(NO_3)_2$ as a precursor. After drying, the samples were pressed into thin wafers (<1 mm) and calcined at 973 K in air for 16 h prior. Reduction of the catalysts was accomplished by holding the catalysts in a reaction mixture containing 5 Torr CH_4 and 15 Torr H_2O for 4 h at 873 K.

Rates for steam reforming of methane were measured by placing the catalysts into a $(1/4)$-inch quartz tubular reactor which has been described in previous publications [9–11]. The total pressure in the reactor was maintained at one atmosphere, but the partial pressures of CH_4, H_2O, and He could be controlled by the flow rates to the reactor. Water vapor was fed to the reactor by bubbling He through deionized, distilled water. In this study, we held the partial pressure of water fixed at 15 Torr and varied only the CH_4 partial pressure. Differential conditions were maintained for all measurements, the methane conversions typically being less than 1%, so that equilibrium considerations did not limit conversions. Rates were highly reproducible and remained constant over a period of several hours. Product analysis (CO_2 and CO) was performed with an on-line Hewlett-Packard 5730A gas chromatograph, equipped with a methanator and FID detector. For the model catalysts, all the reported rates have been normalized to the external surface area of the wafers since this is comparable to the surface area of the precious metal. For the porous catalysts, rates were normalized to the weight of the catalyst.

3. Results

The effect of calcination temperature on the reducibility of ceria has been examined previously in studies of CO-oxidation rates over the model, supported Pd catalysts [9]. As described in section 2, the ceria films in that study were calcined in air for 1 h to increasingly higher temperatures, from 575 to 1675 K. XRD measurements demonstrated that the ceria films had the fluorite structure in all cases; but the crystallite size, as measured by the diffraction line width, increased with calcination temperature [9]. In all cases, 2×10^{15} Pd/cm^2 were added by vapor deposition only *after* calcination of the ceria. The Pd particle sizes, as determined from dispersion measurements using CO-oxidation rates under conditions where the presence of ceria was not important, were approximately 2.5 nm for each of the catalysts.

Figure 1 reproduces CO-oxidation results for three of the model catalysts for which the ceria had been calcined to 575 K (10 nm ceria crystallites), 1175 K (30 nm crystallites) and 1675 K (70 nm crystallites) [9]. Prior to the addition of Pd, rates were so low on the ceria itself that we were unable to measure any conversion of CO under the conditions of our study. The rates in figure 1 were measured as a function of CO pressure at 515 K in 0.3 Torr of O_2 and can be described in terms of two processes, one which is inverse, first-order in CO, and one which is zeroth-order in CO. For the ceria calcined at 1675 K, only the inverse, first-order process was observed. The zeroth-order process was easily observed in the 575 K sample, but was significantly diminished following calcination to 1175 K. A more detailed study showed that the loss of the zeroth-order process occurs sharply in the 1075–1275 K temperature range [9].

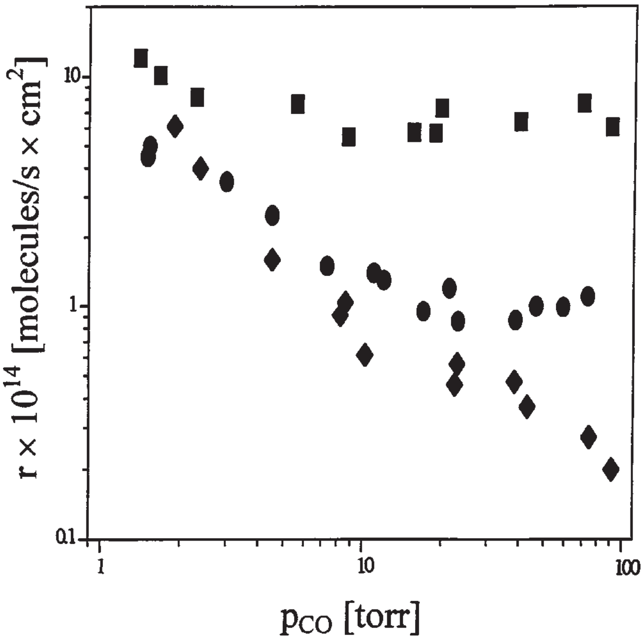

Figure 1. Specific rates for CO oxidation on model, ceria-supported Pd catalysts at 515 K as a function of CO pressure for a fixed O_2 pressure of 0.3 Torr [9]. The ceria films were first calcined in air for 1 h to 575 K (■), 1175 K (●) or 1675 K (◆), prior to vapor deposition of 2×10^{15} Pd/cm^2. Under these conditions, no reaction was observed on ceria in the absence of Pd.

These same three catalysts were examined for steam-reforming activity, with rates shown in figure 2 for partial pressures of H_2O and CH_4 of 15 Torr each. Also shown in figure 2 are steam-reforming rates measured on Rh/ceria and Pt/ceria catalysts (for which CO-oxidation rates have also been reported previously [11]), prepared in the same manner as the Pd catalysts on ceria films calcined to 575 K, with 4×10^{15} M/cm^2. While $H_2O : CH_4$ ratios of one can result in coking [13–16], we did not observe deactivation under our reaction conditions. In all cases, CO_2 was the main product, with only trace amounts of CO observed. As mentioned earlier, no reaction was observed on the ceria films without the addition of one of the precious metals.

The results in figure 2 lead to several interesting conclusions. First, the calcination temperature for the ceria had a critical impact on the activity of the catalysts for steam reforming. Rates on the Pd/ceria catalyst for which ceria had been calcined to 1175 K were 100 times lower than on

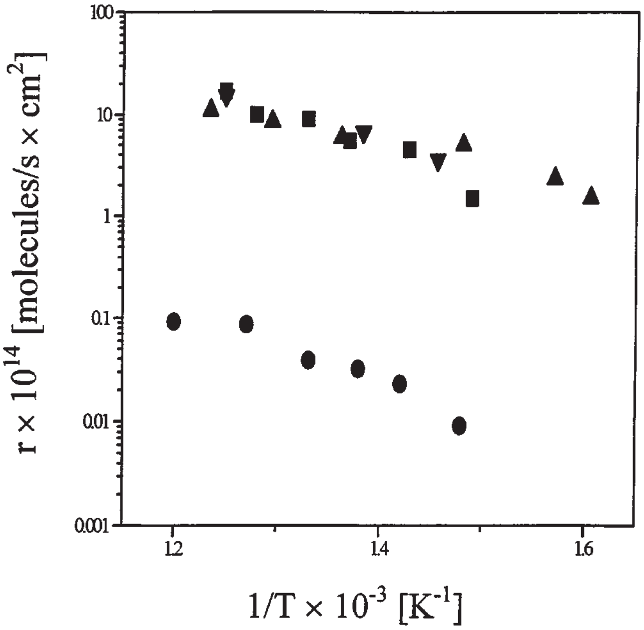

Figure 2. Arrhenius plot for steam reforming of methane over ceria-supported Pd (■), Pt (▼) and Rh (▲) catalysts in which the ceria was calciled at 575 K prior to the vapor deposition of the precious metals. Specific rates (•) for Pd/ceria in which the ceria was calcined to 1175 K are also shown. Data were taken with 15 Torr H_2O and 5 Torr CH_4.

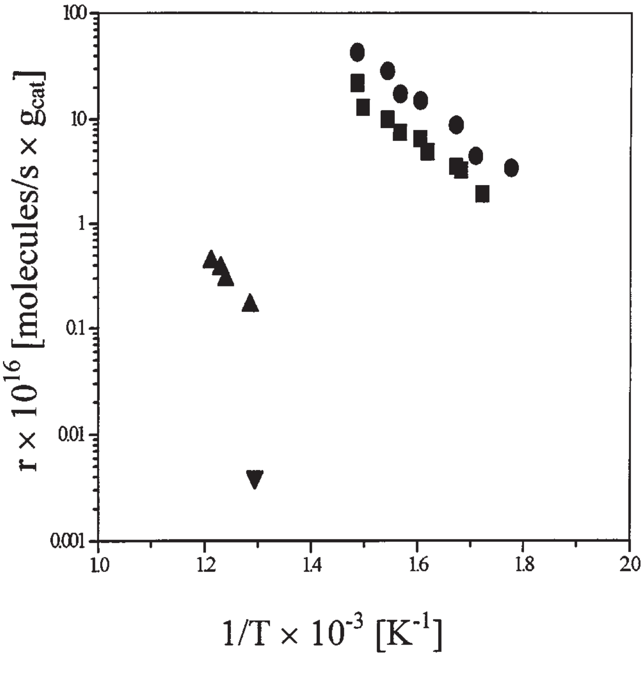

Figure 3. Arrhenius plot for steam reforming of methane over porous catalysts prepared by impregnation of $Pd(NO_3)_2$. Results are shown for 1% Pd on ceria (■), 10% Pd on ceria (•), 10% Pd on silica (▼) and pure ceria (▲). Data were taken with 15 Torr H_2O and 5 Torr CH_4.

the 575 K catalyst. The activation energy of ~18 kcal/mol was approximately the same on both of these catalysts, suggesting that the number of active sites, not the nature of those sites, had changed. No data is shown for the Pd/ceria catalyst for which the ceria had been calcined to 1675 K because no rates were observable on that sample, even at the highest reaction temperature (825 K). Since the lowest measurable rate was $\sim 5 \times 10^{11}$ molecules/(s cm^2), the activity of the 1675 K sample was at least 1000 times lower than the activity of the 575 K sample.

Second, the rates on the Pd/ceria, Pt/ceria, and Rh/ceria catalysts were essentially the same for ceria calcination at 575 K. Identical rates were observed previously on these three catalysts for the zeroth-order process in CO oxidation [11] and for the water–gas-shift activity [10]. For those reactions, it was argued that oxygen transfer from the ceria to the precious metal limited the reaction rates, at least in part. However, since the absolute rates for the water–gas-shift reaction on these catalysts are considerably higher than the steam-reforming rates, for the same partial pressure of water, there must be factors other than simple oxygen transfer involved. One possibility is that oxygen coverage is required on the Pd for the steam-reforming reaction, so that oxygen transfer is limiting, but comparison of rates for the two reactions is not appropriate.

The two observations listed above, taken together, imply a mechanism for steam reforming over the ceria-supported metals similar to that described in section 1 for the water–gas-shift reaction. Methane reacts on the metal sites, causing a reduction of ceria; water, in turn, reoxidizes the ceria. High-temperature calcination deactivates the ceria, so that the transfer of oxygen from ceria to the precious metal cannot occur. The fact that rates on the Rh/ceria and Pt/ceria catalysts are so similar to those on the Pd/ceria catalyst suggests that transfer of oxygen in some way limits the reactivity of these catalysts.

Finally, we also measured steam-reforming rates on conventional, high-surface-area, Pd/ceria and Pd/silica catalysts. Figure 3 shows the rates measured in 15 Torr H_2O and 5 Torr CH_4 for ceria, 10% Pd/silica, 1% Pd/ceria, and 10% Pd/ceria. First, the activity of the Pd/silica catalyst was negligible. We were unable to measure any conversion in the temperature range used for the Pd/ceria catalysts. By extrapolating the data for the 10% Pd/ceria catalyst, we estimate that the Pd/ceria catalyst had an activity that was at least 10^5 times that of the Pd/silica, demonstrating that Pd, by itself, is not an active catalyst for this reaction.

Second, while ceria showed some activity, the rates were again so low that they could not be easily measured in the same temperature range used for the Pd/ceria catalysts. Clearly, rates on Pd/ceria catalysts must occur through a bifunctional mechanism. Rates on the 10% Pd catalyst were roughly three times higher than those on the 1% Pd catalyst, consistent with an increased Pd–ceria contact area. The fact that both Pd/ceria catalysts showed an activation energy of approximately 18 kcal/mol, the same value we observed for the model catalysts, implies that the reaction mechanism is not affected by metal loading or catalyst preparation methods. In agreement with this, specific rates on the 1% Pd/ceria are close to those measured on the 575 K, model Pd/ceria catalyst if one assumes a Pd dispersion of one with a surface density of 10^{15} Pd/cm^2 and uses only the Pd surface area to estimate rates.

4. Discussion

The results shown here have interesting implications for both automotive and steam-reforming catalysis. First, the reforming rates that we observed for methane on the ceria-supported catalysts are high enough to be significant for automotive applications. Given that one should expect rates for larger hydrocarbons to be even higher than that for methane, it would appear that hydrocarbon reforming could contribute to removing hydrocarbons from automotive exhaust streams in reducing environments [16–18]. Furthermore, because the reforming reactions produce hydrogen, a very effective reductant for NO [2], reforming should be very desirable.

It is well known that deactivation of automotive, emissions-control catalysts can occur through the loss of the oxygen-storage capacity (for a comprehensive review, see [3]). The deactivation has usually been explained as being due to a loss in the contact between ceria and the precious metal. However, recent work in our laboratory has suggested that the reducibility of ceria is strongly structure sensitive, so that deactivation appears to be due, at least in part, to the loss of ceria reducibility [9,10]. The present results for steam reforming confirm the earlier work. High-temperature calcination strongly affects the reducibility of ceria and deactivates the catalyst for methane reforming. One implication of the present work is that steam reforming might be an excellent test reaction for monitoring the oxygen-storage properties in automotive catalysts. Because the reaction network and gas composition under operating conditions in an automotive catalyst are complex, evaluation of oxygen storage arising from the oxide component can be difficult [19]. For steam reforming, the activities of both the precious metals and the ceria by themselves are negligible, so that steady-state rate measurements may prove to be informative in evaluating the effectiveness of catalyst formulations.

It is also interesting to compare the rates we have observed on the Pd/ceria catalysts to conventional Ni catalysts, which are used commercially in steam reforming [20–26]. Rostrup-Nielsen [20] reported a turnover frequency of 0.65 CH_4/(s site) on Ni for reaction at 773 K and a methane pressure of 75 Torr. If we assume the reaction is first-order in methane and that there are 10^{15} sites/cm^2 on our model Pd/ceria catalysts, the turnover frequency for our Pd/ceria catalyst at this temperature and pressure is $\sim$5.0 CH_4/(s site), almost 10 times that reported by Rostrup-Nielsen for Ni. Since Ni is considered to be one of the best catalysts for this reaction, the observation that one gets comparable or even higher rates on ceria-supported Pd catalysts is of interest. Obviously, replacing Ni with Pd is probably not desirable in most applications. The high temperatures and high steam pressures required for commercial applications are likely to cause deactivation of Pd/ceria. However, it seems probable that Pd/ceria catalysts may not be as susceptible to coking, so that some specialty applications might be found for these materials [12]. In our studies of Pd/ceria model catalysts, we observed stable operation for $H_2O:CH_4$ ratios of one, conditions which can cause deactivation of Ni catalysts [13–16]. Finally, it should be noted that ceria has been reported to promote reaction on Ni as well [27].

There is considerable mechanistic information on the steam-reforming reaction over Ni. Beebe and coworkers have argued that steam-reforming rates on Ni are limited by the dissociative adsorption of methane [21]. Reaction appears to occur mainly on metallic Ni, since methane activation on the oxide occurs at a much lower rate [24]. However, extrapolation of these ideas to precious metals like Pd and to ceria-supported catalysts does not appear to apply. First, it has been argued that, over Pd, methane oxidation, and therefore the activation of methane, involves reaction on the oxide [28,29]. Second, our model-catalyst studies showed essentially identical rates for Rh/ceria, Pt/ceria, and Pd/ceria for ceria calcination at 575 K. Because one should not expect dissociation to occur at exactly the same rate on all of these metals, this second observation would suggest that a process other than dissociation of methane, such as oxygen transfer from the ceria to the precious metals, limits the reaction.

As discussed in some of our previous publications [7,10,11], understanding the interaction between precious metals and ceria is a very interesting and complex problem for which the structure of ceria plays a critical role. The present results confirm our earlier observations and further demonstrate how large these support effects can be.

5. Summary

The bifunctional mechanism involving oxygen from ceria reacting with a reductant on the precious metal, previously observed for the CO-oxidation and water–gas-shift reactions on ceria-supported precious metals, can also be observed for steam reforming of methane. Specific rates on these catalysts can approach and even exceed those found on Ni. However, the reaction is strongly dependent on the nature of the ceria and high-temperature calcination of the ceria eliminates its capability to donate oxygen.

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