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Comparison of Monolith-Supported Metals for the Direct Oxidation of Methane to Syngas[1]

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The partial oxidation of CH_4 in O_2 near atmospheric pressure to produce syngas was investigated on monolith-supported Rh, Ni, Pt, Ir, Pd, Pd–La_2O_3, Fe, Co, Re, and Ru catalysts in an autothermal flow reactor at residence times of ~10 msec (GHSV ~ 100,000 hr^{-1}). Optimal CH_4 conversion and CO and H_2 selectivities of 0.89, 0.95, and 0.90, respectively, were achieved on Rh at 1000°C with no loss in activity over many hours. Ni showed similar conversion and selectivities but deactivated. Experiments with up to 25 vol% H_2O added to the feed showed little evidence of the occurrence of steam reforming and water–gas shift reactions. Pt and Ir sustained stable reactions but at lower selectivities and conversion than Rh or Ni. Pd, Pd–La_2O_3, and Co deactivated rapidly, while Re, Ru, and Fe would not sustain autothermal reaction. Ni and Re deactivated by volatilization and metal loss, while Pd–La_2O_3 deactivated by carbon formation, and Pd deactivated by a combination of metal loss and carbon formation. Pd produced up to 14% selectivity to C_2H_4 and C_2H_6, Pd–La_2O_3 up to 5%, Pt ~1%, and other metals less than 0.2%. © 1994 Academic Press, Inc.

INTRODUCTION

We have recently shown that high selectivities to CO and H_2 (syngas) can be obtained by the direct oxidation of CH_4 with O_2,

$$CH_4 + \tfrac{1}{2} O_2 \rightarrow CO + 2\,H_2, \qquad [1]$$

over Rh-coated ceramic monolith catalysts with nearly complete conversion of CH_4 at contact times of less than 0.01 sec (1). These experiments were carried out in a steady-state flow reactor which operated autothermally (~1000°C) with a feed temperature of ~25°C. This process has great promise to replace the endothermic and slow steam reforming process for production of chemicals from natural gas through syngas intermediates.

This work followed similar experiments in producing CO and H_2 from CH_4 and O_2 in heated tubes using Rh, Ru, Pd, Pt, and Ni catalysts supported on various powder oxide supports at contact times of nominally 0.1 sec (2–4). However, in those experiments the initial reactions were believed to produce H_2O and CO_2,

$$CH_4 + O_2 \rightarrow CO + H_2O \qquad [2]$$

$$\rightarrow CO_2 + H_2O, \qquad [3]$$

with reforming reactions with excess CH_4,

$$CH_4 + H_2O \rightarrow CO + 3\,H_2 \qquad [4]$$

$$CH_4 + CO_2 \rightarrow 2\,CO + 2\,H_2, \qquad [5]$$

ultimately producing nearly equilibrium yields of CO and H_2 at the longer contact times. The same reaction sequence was proposed to explain approximately equilibrium yields for the production of syngas from CH_4, H_2O, and O_2 over Pt/Pd coated monoliths in a high-pressure autothermal reactor at contact times of 0.02 sec (5). These papers are consistent with the idea that most noble metal catalysts gave qualitatively similar conversions and selectivities which in the best cases were very close to thermodynamic equilibrium (ignoring carbon formation).

However, we found that at short contact times using monoliths, Rh was much superior to Pt in producing syngas, and we showed that this could be explained by the instability of adsorbed OH on Rh which reduces the formation of H_2O (1) and the high mass transfer characteristics of monoliths at very high flow velocities (6).

In this paper we compare activities and selectivities of nine different noble metals in syngas formation using an autothermal reactor. The objectives are to determine which metals are most suitable for the process, what catalytic and materials properties of metals are required to produce syngas, and what reaction steps account for the differences between metals.

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APPARATUS AND PROCEDURE

Experiments were carried out in an insulated 18-mm-ID quartz tube flow reactor containing a metal-coated monolith catalyst which was a 17-mm-diameter, 10-mm-long foam of α-Al_2O_3 with nominal 45 pores per linear inch, as indicated in the inset in Fig. 1a.

The catalysts were prepared by coating the monolith with the desired metal from concentrated salt solutions which were added dropwise to the monolith, allowed to dry overnight, and calcined. Metal acetates (rhodium acetylacetonate, palladium acetate, and nickel acetate) were calcined in He at 600°C for 6 h, while metal chlorides and nitrides (all other metals used) were heated in He at ~800°C for 8 h. After calcining, the catalysts were reduced in H_2 at 650–700°C for at least 6 h. The color of the reduced catalysts ranged from light gray with a metallic luster (Pd and Ir) to dark gray (Ni). Metal loadings were calculated from the masses of the coated and uncoated monoliths.

Straight channel extruded ceramic monoliths ~10-mm long were positioned before and after the foam monolith to reduce radiation losses. The catalyst and radiation shields were sealed in the quartz tube by silica–alumina cloth, and the reactor was insulated by wrapping the quartz tube in high-temperature insulation. Preheating of the reactants to up to 300°C was achieved by heating tape wound around the tube upstream of the catalyst.

The temperatures of the front (upstream) and back (downstream) sides of the catalyst were measured by Pt–Pt/Rh thermocouples placed between the catalyst and the radiation shields. The temperatures reported in this paper and used for equilibrium calculations are the downstream temperatures. Since at the downstream edge of the catalyst the product gas and the catalyst are at the same temperature, the radial position of the thermocouple is not as critical as at the upstream edge where incorrect positioning (e.g., in a pore) can result in measurement of the gas temperature, which is lower than the catalyst temperature. The downstream temperature was typically within 100°C of the calculated adiabatic temperature. Optical pyrometer measurements were consistent with these temperatures.

Flow rates of high purity O_2 and CH_4 (99.0%), as well NH_3 and air, were controlled by mass flowmeters with an accuracy of better than ±0.05 slpm. For experiments in which steam was added to the feed, water was pumped through a long, thin tube inserted into the preheat section of the reactor that permitted the water to be completely vaporized before reaching the catalyst.

Product gases were analyzed by a Carle 510 gas chromatograph (GC) consisting of two columns, a Porapak T and a Molecular Sieve 5A, in series which were capable of separating small molecules, and a third column, a Hayesep R, which was used to separate C_{2+} compounds when necessary.

Ignition and Shutdown

In all experiments the catalysts were operated autothermally in that the heat generated by the reaction was sufficient to sustain reaction. The autothermal steady state was achieved by igniting the catalyst with an NH_3/air mixture, which was preheated using a Bunsen burner, and then switching to CH_4 and O_2. It was necessary to use NH_3 (ignition temp ≥200°C) for light-off since the CH_4/air system can only be ignited by heating above 600°C.

Ignition in the NH_3 in air mixture occurred at between 200 and 350°C depending on the metal (see Table 1), and was indicated by a rapid increase in temperature to between 600 and 1080°C.

Once the catalyst had ignited, CH_4 and O_2 flows were increased, the air flow rate was decreased, and the NH_3 was shut off, keeping fuel/O_2 ratio constant near the syngas ratio. The total flow rate was then adjusted to 4 slpm (maintaining 0.2 slpm of air), the pressure was increased to 6 psig, and the system was allowed several minutes to achieve steady state before samples were analyzed. At 4 slpm, the residence time is ~10 msec (at 1100 K, 1.4 atm, 0.7 void fraction) and the GHSV is $1 \times 10^5\ h^{-1}$.

Shutdown of the reactor was accomplished by turning off O_2 and air before CH_4.

Calculation of Conversion and Selectivities

Since nitrogen was not consumed or formed in the reaction, the N_2 peak was used as a calibration for mass balances. Methane conversion, CO and C_2 selectivity (on a carbon atom basis) are defined as

$$CH_4\,\mathrm{conv} = \frac{\Delta CH_4}{CH_{4,\mathrm{in}}} = \frac{F_{CH_4,\mathrm{in}} - F_{CH_4,\mathrm{out}}}{F_{CH_4,\mathrm{in}}} \quad [6]$$

$$S_{CO} = \frac{F_{CO}}{\Delta CH_4} = \frac{F_{CO}}{F_{CO} + F_{CO_2} + 2(F_{C_2H_4} + F_{C_2H_6})} \quad [7]$$

$$S_{C_2} = \frac{F_{C_2}}{\Delta CH_4} = \frac{2(F_{C_2H_4} + F_{C_2H_6})}{F_{CO} + F_{CO_2} + 2(F_{C_2H_4} + F_{C_2H_6})}. \quad [8]$$

The quantities of water and hydrogen were determined from oxygen and hydrogen atom balances instead of using the hydrogen peak measured by the GC.

The conversions and selectivities shown in Figs. 1 and 2 are believed to be accurate to within ±1%. Carbon atom balances closed to within ±4%.

TABLE 1

Comparison of Metals

Metal and loading (wt%)	Ignition temperature (°C) in NH_3/air	Reaction temperature (°C)	$\frac{\Delta CH_4}{CH_{4,in}}$	S_{H_2}	S_{CO}	Stability	Catalyst changes	Coke formation
4% Rh	~200	~930	.80	.90	.96	Stable		No
3% Ni	~340	~730–830	.80	.91	.93	Deactivates slowly	Formation of oxide and aluminate; volatilization	No
2.5% Ir	~220	~920	.73	.85	.94	Stable		NO
4.7% Pt	~200	~1130	.67	.78	.94	Stable		Some
3% Co	~295	~1000	.20	.14	.66	Deactivates	Formation of aluminate	No
3.5% Pd–La_2O_3[a]	~320	~1200	.56	.57	.83	Deactivates	Pore blockage	Yes—very heavy
0.5% Pd[b]		~1270	.52	.53	.72	Deactivates	Volatization	Yes
4% Re						Deactivates quickly	Volatization	No
5.5% Ru	~265					Extinguished in CH_4	Phase change	No
6.5% Fe						Extinguished in CH_4	Phase change	Some

Note. All conversions, selectivities, and reaction temperatures at CH_4/O_2 = 2.0 and 4 slpm, with 300°C feed, except as noted.

[a] 25°C feed.

[b] 2.5 slpm, 25°C feed

RESULTS

Conversions and Selectivities

A comparison of CH_4 conversion, CO and H_2 selectivities, and catalyst temperature for Ni, Rh, Ir, and Pt with 25°C feed temperature is shown in Fig. 1. Conversion increased with decreasing CH_4/O_2, while the CO selectivity was nearly independent of composition between CH_4/O_2 ratios of 1.6 to 2.0. H_2 selectivity exhibited broad and shallow maxima for all catalysts except on Pt, where it decreased rather strongly with increasing CH_4/O_2.

CH_4 conversions on Ni and Rh were nearly identical at small CH_4/O_2 (~1.6), but selectivities differed significantly. Rh was more selective to CO than Ni by 4%, whereas Ni exhibited a higher H_2 selectivity by 2%. Pt and Ir showed consistently lower conversion and selectivities than either Rh or Ni.

The highest autothermal reaction temperatures were measured on Pt and Ir, as shown in Fig. 1d. This is as expected since these catalysts are less selective to the less exothermic partial oxidation reactions.

Figure 2 shows the conversion, selectivities, and temperature for Rh, Ni, Pt, and Ir with 300°C feed. For all catalysts except Ni, conversion and H_2 selectivity were higher by several percent while the CO selectivity was nearly constant when compared with the room temperature feed data in Fig. 1. For Ni, the CO selectivity increased by several percent, H_2 selectivity decreased by ~1%, and conversion was unchanged. We believe that this loss in activity observed on Ni is due to metal loss and compound formation.

As shown in Fig. 2d, catalyst temperatures increased ~80°C when the feed was preheated 300°C. Temperatures for Ir are not shown since the thermocouple was improperly positioned in this experiment. Again, higher reaction temperatures are observed on catalysts that are less selective.

Characteristics of Catalysts

Used catalysts were examined for signs of carbon, changes in color, and agglomeration or migration of the metal. Carbon was most often observed as a brown soot-like deposit on the tube walls downstream of the catalyst. In cases of heavy carbon formation, the downstream edge of the catalyst was covered by a black deposit. The catalyst surface was examined with an optical microscope to determine if sintering or volatilization of the metal had occurred.

The ignition, stability, and appearance of the catalysts is described below and summarized in Table 1.

Pt, Rh, and Ir

Pt, Rh, and Ir exhibited fairly similar behavior except that Rh gave consistently higher conversions and selectiv-

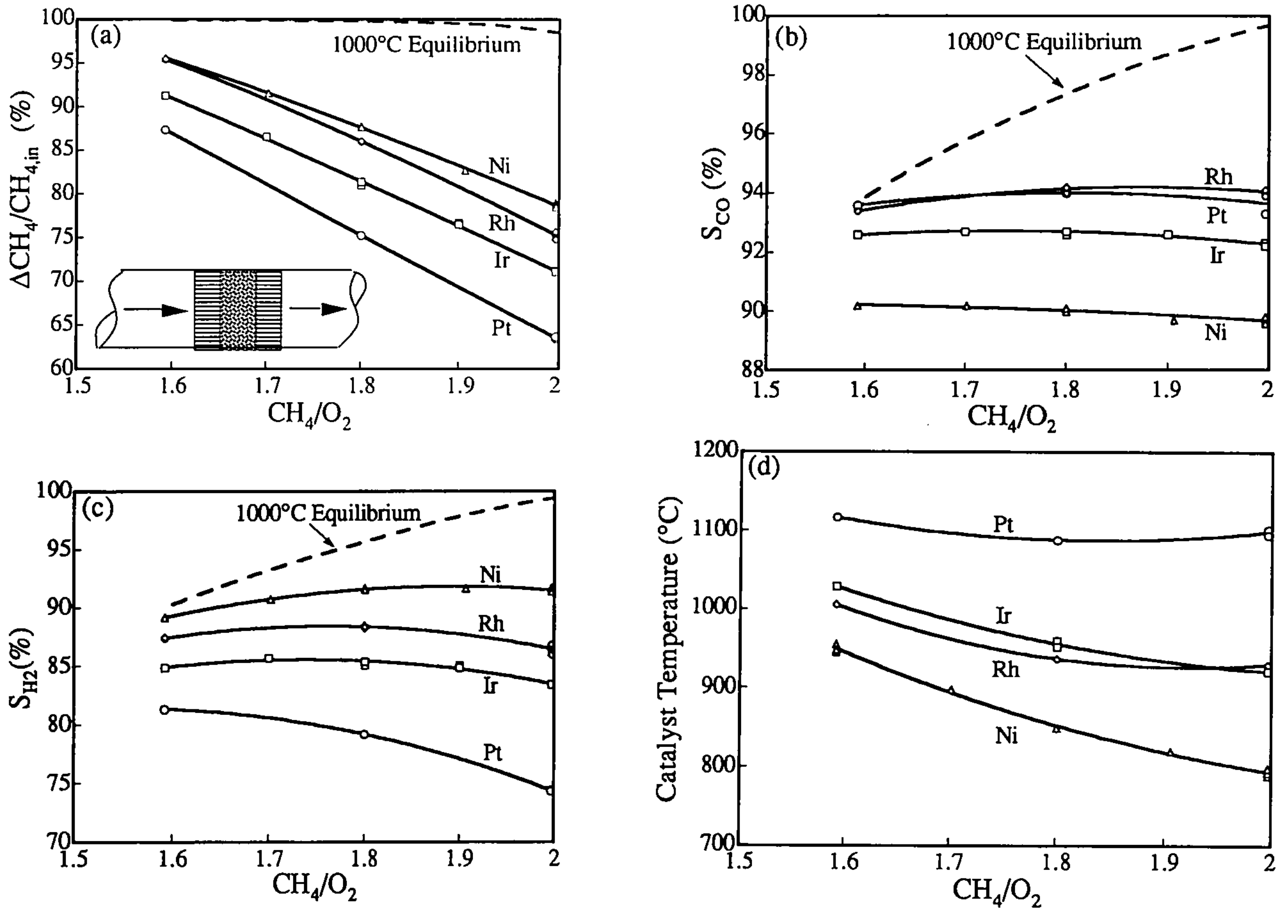

FIG. 1. Comparison of (a) CH_4 conversion, (b) CO and (c) H_2 selectivities, and (d) measured catalyst temperatures for methane oxidation over alumina foam monoliths coated with 4% Rh, 4.7% Pt, 3% Ni, and 2.5% Ir at room temperature feed. Also shown in the inset of (a) is a sketch of the catalyst with radiation shields.

ities. The ignition temperature of the NH_3/air mixture was approximately 200°C on each of these catalysts, and catalytic activity was stable after an activation period of 3 h. During the activation period, CH_4 conversion and H_2 selectivity on freshly prepared samples typically increased with time by several percent, while the CO selectivity was nearly steady.

The color of the catalysts changed from metallic or medium gray of the fresh catalysts to a lighter gray on the used catalysts, and the used Ir catalyst lacked the luster of the unused sample. It is believed that the changes in color are due to sintering of the metal into larger particles, exposing Al_2O_3. Large crystals of metal (~100 μm) were observed on the used catalysts.

No coke formation was observed on the Rh and Ir catalysts after running at CH_4/O_2 ratios of 1.5–2.0 for 8 h on Rh and 11 hr on Ir. However, on Pt some coke was visible on the tube wall downstream of the catalyst, and ~1% C_2 selectivity was measured after ~1 hr of operation. All of these catalysts appeared to run indefinitely without severe deactivation.

Ru and Fe

Neither of these catalysts was active for the syngas reaction. Ru and Fe readily ignited with the NH_3/air mixture at ~265°C, and the temperature rose to ~1070°C, but they extinguished as the NH_3 flow was decreased and CH_4 increased.

Within 30 sec of ignition, the downstream edge of the Ru catalyst turned a tan–gold color. As the NH_3 flow was decreased, the catalyst returned to its original gray color and extinguished.

Likewise, the back of the Fe catalyst turned a reddish-brown color, and the front showed a black coating indicative of coke.

Re

The extremely high temperatures observed on the Re coated monolith precluded a thorough study of this catalyst, although the high temperatures indicated low selectivities to CO and H_2. The temperature of the reaction of the NH_3/air mixture was ~1010°C (compared with 875°C

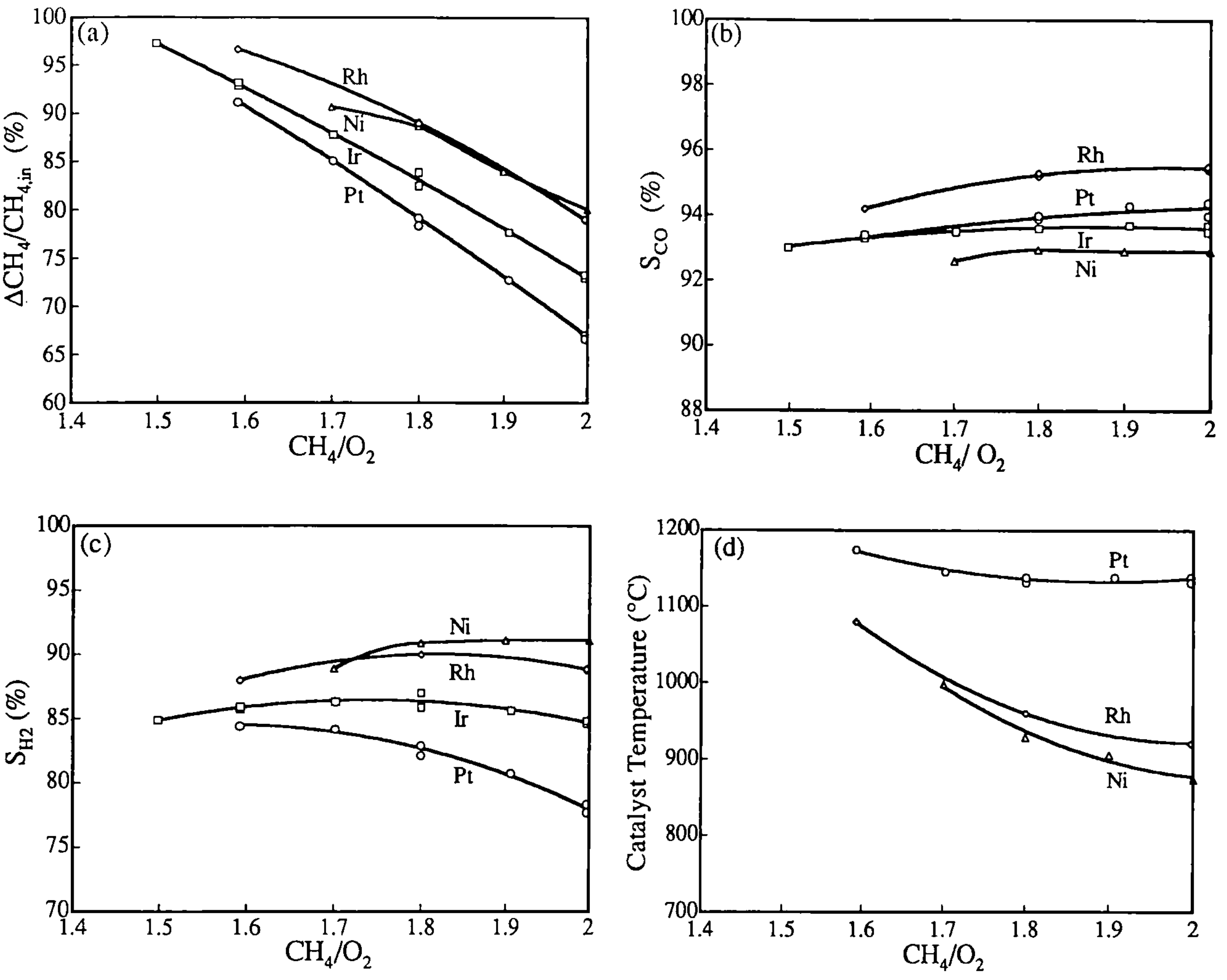

FIG. 2. Comparison of (a) CH_4 conversion, (b) CO and (c) H_2 selectivities, and (d) measured catalyst temperatures for 300°C feed.

on Pt). Upon shutting off the NH_3 and increasing the CH_4, the temperature jumped to ~1430°C and the pressure increased. The limits of safe operation were exceeded, and the reactants were shut off. The used catalyst was white (no metal remaining), and the tube wall downstream of the catalyst was coated with a highly reflective red material typical of Re oxides.

Pd

Pd coked heavily and deactivated. Conversion decreased from 52 to 28% and H_2 selectivity decreased from 53 to 41% over ~2.5 hr. C_2 selectivity also decreased with time from 14 to 6%, but it was still higher on Pd than any other catalyst (see below).

After running ~10 hr, the catalyst and tube wall downstream of the catalyst were coated with coke and the catalyst showed signs of metal loss. A shiny coating of silvery metal on the downstream edge of the catalyst and on the downstream radiation shield indicated that Pd migrated from the front of the catalyst, which after reaction was a dull gray. Due to the exceptionally high reaction temperature on Pd, all results were obtained at 2.5 slpm with 25°C feed in order to maintain the temperature within safe operating limits.

Pd–La_2O_3

As with Pd, Pd–La_2O_3 deactivated substantially after several hours of operation and had a very high autothermal temperature.

CH_4 conversion decreased from 45 to 40%, H_2 selectivity decreased from 63 to 49%, and CO selectivity decreased from 86 to 79%, but C_2 selectivity increased 10-fold to ~3.5% in this period. Coke formation was extensive on the tube wall, part of the front of the catalyst, and the back of the catalyst where the carbon deposit appeared to be filamentous.

Co

Co underwent an obvious physical change during ~1.5 hr of reaction in CH_4/O_2, as indicated by a color change from dark gray to bright blue on the front of the catalyst. The blue portion is associated with a tetrahedral Co compound, probably $CoAl_2O_4$. It appeared that the blue regions of the catalyst were not lit.

It was difficult to sustain the reaction on the catalyst at flow rates approaching 4 slpm. Up to 3 slpm, only the catalyst was lit, however, at higher flow rates the downstream radiation shield glowed due to metal deposition on the radiation shield, and significant C_2's were measured (3.5% C_2H_4 sel.).

Runs performed without radiation shields yielded lower CH_4 conversion, lower CO and H_2 selectivities, and no C_2's. Conversion and selectivities decreased with increasing flow rate, which is opposite the trend observed for Pt catalysts.

Ni

Of all the catalysts that were active for syngas formation, Ni required the most preheat to ignite (ignition temperature ~340°C).

The appearance of the catalyst changed significantly after several hours of operation and analysis by XPS confirmed a change in the oxidation state and concentration of Ni. We observed after 3 hr of operation, a light blue compound that had formed over the entire catalyst surface and a yellow–green compound that had formed on the back of the catalyst. With increasing time on stream, the concentration of Ni on the front of the catalyst (and on the back to a lesser extent) decreased until after 22 hr, less than 0.1 wt% Ni remained on the front of the catalyst. We observed multiplet splitting of the Ni XPS peak characteristic of Ni bonded to O, which has been associated with $NiAl_2O_4$ and NiO (3).

In addition to compound formation and metal loss, the conversion and H_2 selectivity decreased by ~2% over 22 hr. Other workers have reported unstable activity with Ni catalysts as well (7).

C_2 Formation

There has been much interest in the conversion of methane to C_2's by oxidative coupling. A heterogeneous/homogeneous mechanism has been suggested in which methyl radicals are formed on the surface by reaction between CH_4 and adsorbed oxygen species which then desorb and recombine in the gas phase.

Hickman, *et al.* (1) observed less than 0.1% selectivity to C_2H_4 and C_2H_6 on 10 wt% Rh for CH_4/O_2 values of 1.6 to 2.0, and ~4% C_2 selectivity on 11 wt% Pt for the same range. C_2's were produced only when O_2 was used as an oxidant and air gave negligible C_2's.

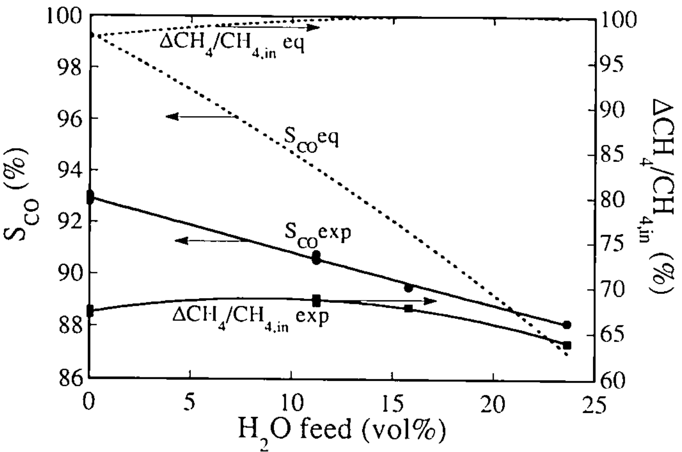

FIG. 3. Comparison of equilibrium (dashed lines) and experimental (solid lines) conversion and CO selectivity as the quantity of steam in the feed is increased. Temperature was maintained at 935°C, and the CH_4, O_2, and N_2 flows were held constant at 2.18, 1.10, and 0.725 slpm, respectively.

We measured C_2 concentrations in most of these systems and found negligible C_2 formation on all catalysts except Pt, Pd, Pd–La_2O_3, and Co. On Pt a maximum of ~1% C_2 selectivity was observed at CH_4/O_2 of 1.6. The highest selectivity to C_2's we attained was ~14% on Pd. Approximately 3% C_2 selectivity was observed on Pd–La_2O_3. For Pd and Pd–La_2O_3, selectivities varied substantially with time. The C_2H_4/C_2H_6 ratio was typically 2 to 3.

Although C_2's were measured using Co, further experimentation showed that this was due to reaction on the downstream radiation shield, as opposed to reaction on the catalyst.

Effect of Steam

We also examined the effect of adding H_2O to the feed on the conversion and selectivity. An increase in conversion of CH_4 and a decrease in CO selectivity should indicate a contribution from steam reforming while constant selectivity should indicate mainly direct oxidation. An increase in CO selectivity with no change in CH_4 conversion would indicate the water gas shift reaction.

Up to 24 vol% of steam was added while maintaining a constant feed flow rate of CH_4, O_2, and N_2 at 4 slpm, and the amount of preheat was adjusted to maintain a constant catalyst temperature of 935°C. At the highest steam flow rate, the H_2O/O_2 ratio was approximately unity.

As shown in Fig. 3, the experimental CH_4 conversion was nearly constant at ~65% for the entire range of H_2O concentrations tested. The only discernible trend is a slight *decrease* in conversion as H_2O is added. The equilibrium CH_4 conversion is nearly 100% as shown in the figure.

The experimental CO selectivity dropped slightly from 93 to 89%. Over the same range, the equilibrium CO selectivity decreases from 99 to 87%, and equilibrium is actually *lower* than the observed CO selectivity at 24 vol% H_2O.

These results indicate that steam reforming of the CH_4 does not occur significantly and that CO does not react substantially with H_2O in the water–gas shift reaction. This is in strong contrast to previously reported experiments on Ru and Ni in heated tube reactors at longer contact times. The issue of the approach to equilibrium is considered in some detail in a later section.

DISCUSSION

A successful syngas catalyst requires (1) reaction steps which produce CO and H_2 rather than CO_2 and H_2O, (2) a stable metal surface, and (3) negligible solid carbon formation. We discuss each of these aspects in turn.

Reaction Steps

The CO selectivities are >90% for essentially any catalyst with $CH_4/O_2 > 1.5$ over a wide range of temperatures. Thus, the sequence $C_s + O_s \rightarrow CO_s \rightarrow CO_g$ is highly favored over $CO_s + O_s \rightarrow CO_{2s} \rightarrow CO_{2g}$ because CO_s readily evaporates. The adsorption lifetime of CO is $\sim 10^{-8}$ sec at 1000°C if the heat of adsorption of CO is 30 kcal/mole, which is observed on all of these metals.

However, the H_2 selectivities are strongly dependent on the metal. We showed previously that H_2 formation $2\,H_s \rightarrow H_{2s} \rightarrow H_{2g}$ competes with $H_s + O_s \rightarrow OH_s \rightarrow H_2O_s \rightarrow H_2O_g$, and that the details of these steps depend strongly on the surface (1). On Pt, the activation energy of $H_s + O_s \rightarrow OH_s$ is only 2.5 kcal/mole, while on Rh the activation energy for this step is 20 kcal/mole. Therefore *on Rh the dimerization barrier is lower than the OH and H_2O barriers,* so predominantly H_2 forms, while on Pt, H_{2g} has a higher energy barrier than the H_2O barrier.

The variation in H_2 selectivities between Pt and Rh can be explained simply by the higher heat of adsorption of O_s on Rh than Pt, and similar arguments should hold for the other metals. Pd should produce low H_2 selectivities because Pd and Pt have low heats of adsorption of O_s (~50 kcal/mole). The less noble metals should have higher H_2 selectivities because they all have high heats of adsorption of O_s.

These considerations determine H_2 selectivities only if other reactions with the metal do not deactivate the catalysts. Only for Ni, Rh, Pt, and Ir are catalysts sufficiently stable to attain truly steady state catalytic reaction kinetics.

We believe that homogeneous reactions are negligible in these experiments. This is because we see no evidence of flames, mixtures are nonflammable at these compositions, flow velocities are high, and large catalyst surface areas and small pore sizes efficiently scavenge free radicals which are necessary for homogeneous reactions.

Metal Stabilities

Table 1 summarizes observations on the nine metals. Deactivation will probably occur if catalysts (1) form solid compounds, (2) sinter into very large particles, or (3) volatilize. We have found that for Rh the selectivities and activities are nearly identical for metal loadings between 1 and 15% (1). We interpret this as arising from nearly continuous metal films. Sintering should only be a problem if particles grow such that the total metal area is significantly reduced. Similarly, volatilization is only a problem if a large fraction of the metal evaporates from the catalyst.

Solid compounds such as oxides and aluminates will form with the less-noble metals (Co, Fe, Ni) if they are heated in oxidizing atmospheres. Compound formation should mostly be a problem near the front surface and when the CH_4/O_2 ratio is small at these catalyst temperatures, although their formation conditions depend on gas compositions and temperature and will vary with metal and with position in the catalyst because gas composition and temperature vary down the catalyst. Metal volatilities depend on vapor pressures which range from 10^{-6} Torr on Pd to less than 10^{-11} Torr on Re at 1000°C in the order Pd > Fe > Ni > Co > Pt > Rh > Ru > Ir > Re (8). Volatile oxides and other compounds also produce metal loss, and Ru and Pt have highly volatile oxides while Ni, Fe, and Co have volatile carbonyls. We observed the greatest deactivation due to volatilization for Re, Ni, and Pd. Metal loss is of course closely coupled to syngas selectivity in an adiabatic reactor, and Re and Pd are especially hot because they have poor selectivities as syngas catalysts.

Carbon Deposition

Shown in Fig. 4 is a comparison of measured catalyst temperatures with room temperature feed for the four stable metals along with calculated equilibrium mole fractions of solid carbon as a function of CH_4/O_2. The equilibrium carbon concentration at a given temperature and gas composition was calculated by implementing a computer program that utilized element chemical potentials in a free energy minimization technique. Carbon formation was taken to be crystalline graphite in these calculations. For $CH_4/O_2 \geq 2$, equilibrium predicts graphite formation at any temperature.

Under the conditions of these experiments with room temperature feed of Fig. 1, the formation of graphite is

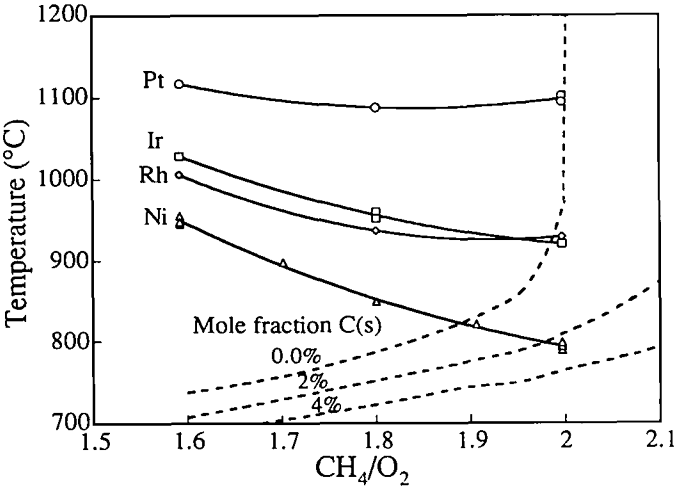

FIG. 4. Measured catalyst temperatures and calculated equilibrium mole fractions of solid carbon as a function of CH_4/O_2.

thermodynamically predicted for CH_4/O_2 ratios of greater than ~1.98 on Rh and Ir and ~1.9 on Ni. In fact, only on catalysts with *higher* reaction temperatures were significant carbon deposits observed (see Table 1). Moreover, the rate of coke formation was greater when the feed was preheated (i.e. higher reaction temperature). This indicates strongly that the generation of coke is not predicted simply by thermodynamically limited formation of graphite.

A major potential cause (and effect) of carbon formation is catalyst deactivation. If reaction and heat generation rates decrease, then the temperature decreases and the system moves downward into the regime of graphite stability in Fig. 4. Carbon formation further deactivates the catalyst, and therefore the process should accelerate. We frequently observed with Pd and several other metals that deactivation originated at either the front or back regions of the monolith and propagated through the catalyst. Particular spots on the catalyst occasionally deactivated, and these cold spots grew to envelope the catalyst.

We observed that Rh and Pt exhibited negligible deactivation or visible carbon formation for operation of many hours, and in other experiments (not shown) these catalysts were stable even when $CH_4/O_2 > 2$ where thermodynamics predicts up to 50% of the carbon feed should form graphite.

Soot deposition on downstream tube walls could occur through formation of carbon particles on the catalyst or through filamentous carbon on the catalyst which breaks off and deposits downstream. Carbon formation from olefins does not appear to be responsible for carbon on walls because in other experiments we find that with C_2H_4 production up to 70%, negligible carbon was deposited either on the catalyst or on the tube walls over many hours.

Approach to Equilibrium

Product compositions approach total thermodynamic equilibrium with respect to gaseous species (32.4% CO and 64.6% H_2 at 1000°C for $CH_4/O_2 = 2$) as indicated by dashed lines in Fig. 1 with negligible CH_4 or O_2 remaining. However, the systems definitely do not attain equilibrium with respect to solid graphite, especially for Rh and Ni which operate at the lowest temperatures (because they approach the syngas equilibrium).

In this section, we compare product compositions with those predicted from thermodynamic equilibrium considerations.

In the water–gas shift (WGS) reaction

$$CO + H_2O \leftrightarrows CO_2 + H_2 \qquad [9]$$

the equilibrium is a function of the selectivity ratios

$$K_{WGS} = \frac{P_{CO_2} P_{H_2}}{P_{CO} P_{H_2O}} = \frac{S_{H_2}(1 - S_{CO})}{S_{CO}(1 - S_{H_2})}. \qquad [10]$$

In Fig. 5a are plotted all experimental points from Figs. 1 and 2 along with K_{WGS}. It is seen that for Rh and Ni most points lie within 20% of WGS equilibrium while points for Pt and Ir deviate by as much as 50%. Note also that Ni deviates in producing *too much* H_2 (or too little CO) while Rh, Pt, and Ir deviate in producing *too little* H_2.

The steam reforming (SR) equilibrium relation is

$$K_{SR} = \frac{P_{CO} P_{H_2}^3}{P_{CH_4} P_{H_2O}}, \qquad [11]$$

and experimental data and K_{SR} are plotted in Fig. 5b for all points in Figs. 1 and 2. All deviate in yielding too much CH_4, but Ni comes close to SR equilibrium while other metals deviated by several hundred degrees or by a factor of more than 10 at fixed temperature. Ni points are pushed closer to SR equilibrium by production of more than equilibrium H_2 in WGS, while for Rh they are pushed away from SR equilibrium by production of too little H_2.

Thus at the ~0.01 sec contact times of these experiments, product compositions are close to those predicted by WGS but not SR. This, of course, does not indicate which rate processes dominate, and we suggested previously that selectivities indicate that direct oxidation initiated by CH_4 pyrolysis

$$CH_4 \rightarrow C_s + 4\,H_s \qquad [12]$$

dominates (1). The deviation from SR equilibrium confirms that total oxidation to produce H_2O followed by SR does not explain these results except possibly for Ni.

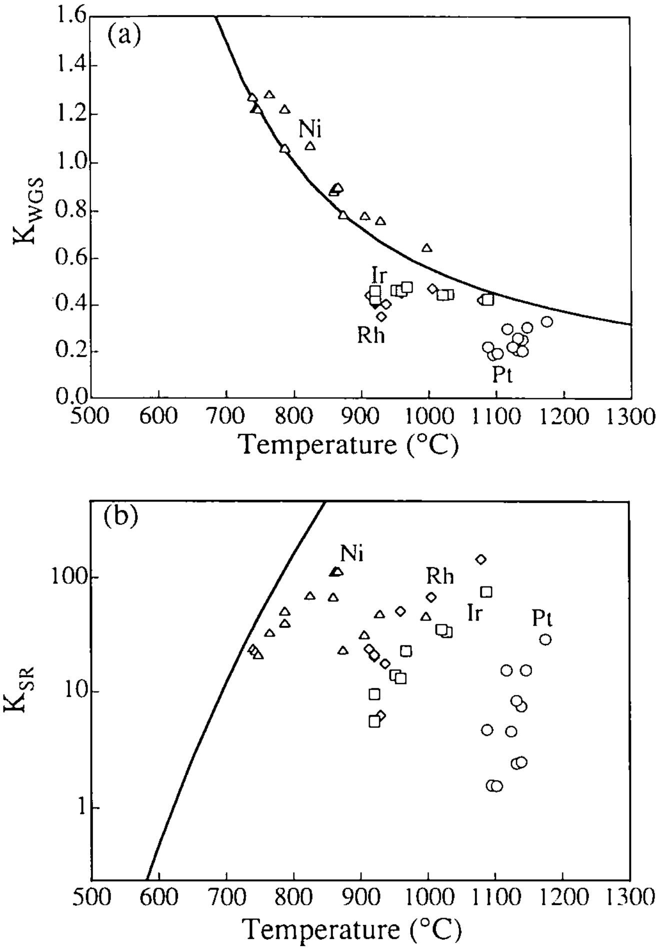

FIG. 5. Experimental equilibrium constants (symbols) and theoretical equilibrium constants (curves) for the (a) water–gas shift reaction and (b) the steam reforming reaction.

The large differences between metals also indicates strongly that product distributions are controlled by *kinetics of individual steps on the catalyst surfaces* which clearly exhibit large variations among these metals.

We note again that this discussion applies only to the four best catalysts. The others were unsuitable because of chemical equilibrium in other reactions: Pd and Pd–La_2O_3 because of carbon formation and others because of vaporization of metal or metal compounds. Note that Re and Pd were unstable because they operated at very high temperatures: the poor selectivities to CO and H_2 produced so much heat that volatilization of the catalysts occurred.

Comparisons with Previous Work

Similar experiments on most of these metals have been carried out with oxide supported powders in heated tube microreactors at longer contact times (2–4, 7, 9, 10). Platinum-group metals gave near equilibrium conversions and selectivities at ~800°C.

In contrast, we observed quite different behavior in comparing metals because our reactor is autothermal and nearly adiabatic, our contact times are shorter, and our temperatures are frequently higher. Therefore, we do not attempt to compare in detail these and our experiments. We note however, that significant disagreement exists in some situations between previous publications.

In heated tube experiments gases (usually diluted) are preheated to the oven temperature, and we suggest that in regions in the catalyst temperatures may be locally much higher than the temperature measured by a thermocouple inserted near the back of the reactor. In several experiments dramatic changes in conversion and selectivities were reported as temperature was varied; their effects may have been caused by ignition and extinction behavior rather than simply as changes in the catalysts. Since most of these experiments measure or infer that H_2O and CO_2 are primary products, temperature variations may be very large even in 5-mm-diameter tubes because the heat of formation of CO_2 and H_2O is -192 kcal/mole versus -8.5 kcal/mole for direct syngas formation. Steam reforming is endothermic by 49 kcal/mole, and this reaction could cool sections of the catalyst even below the oven temperature.

Large reactors must of course operate autothermally and adiabatically, and these conditions cannot be duplicated precisely by a heated tube microreactor. Use of H_2O and O_2 with natural gas in packed beds is used in "autothermal steam reforming," which is a hybrid reactor between steam reforming (H_2O only) and direct oxidation (O_2 only). The autothermal experiments of Hochmuth use both H_2O and O_2 to control temperature and carbon formation. We find that addition of H_2O in our experiments does not increase CH_4 conversions significantly and is not necessary to avoid carbon formation.

SUMMARY

Examination of syngas formation on nine noble metal catalysts on Al_2O_3 monoliths indicates that Rh and Ni are the only metals giving high and stable syngas yields, with Rh exhibiting no measurable deactivation but Ni requiring operation at low temperatures to reduce metal loss. Pt and Ir are stable but give lower syngas selectivities. The other metals appear to have serious problems with deactivation under these operating conditions.

While Rh appears to be the catalyst of choice for syngas reactions, Pt is best for production of olefins by oxidative dehydrogenation, and other metals, oxides, and metals with additives may be optimal for other reactions.

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