Effect of palladium on iron Fischer–Tropsch synthesis catalysts

Mingsheng Luo[a], Robert O'Brien[a] and Burtron H. Davis[a,*]

[a]Center for Applied Energy Research, 2540 Research Park Drive, Lexington, KY 40511, USA

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Studies were conducted to investigate the effect of Pd on the Fischer–Tropsch Synthesis (FTS) selectivity, activity and kinetics as well as on the water–gas shift activity of an iron catalyst. Two palladium promoted catalysts (Pd0.002/Fe100 and Pd0.005/Fe100) were prepared from a base Fe100/Si5.1 (atomic ratio) catalyst. Results of FTS over the two palladium promoted catalysts were compared to those obtained from the K/Fe/Si base catalyst and a Cu/K/Fe/Si catalyst. The results indicate that Pd enhanced the FT activity while the selectivity for CO_2 and CH_4 changed little compared to the results for the base catalyst and the Cu promoted catalyst. Palladium promotion had a negative effect on the C_2—C_4 olefin to paraffin ratio. Pd promotion led to a higher WGS rate than the other two catalysts at high syngas conversions. A higher WGS rate compared to the FTS rate was obtained only for the Pd promoted catalysts. The FTS rate constant for the Pd promoted catalyst is higher than the base catalyst but lower than for the Cu promoted catalyst.

KEY WORDS: Fischer–Tropsch Synthesis; Gas-to-liquid; Palladium; Copper; Potassium; Iron catalyst; Promotion; Pretreatment; Reduction; Syngas.

1. Introduction

Hydrocarbons are produced from CO and H_2 by the Fischer–Tropsch Synthesis (FTS) reaction that can be expressed as:

$$(n/2+1)H_2 + CO \rightarrow CH_n + H_2O (n \text{ ca. } 2) \qquad (1)$$

When an iron catalyst is used for FTS, the water–gas shift (WGS) reaction can also occur. This reaction consumes CO and water that is formed by the FTS reaction to produce additional hydrogen as well as carbon dioxide:

$$H_2O + CO \rightarrow CO_2 + H_2 \qquad (2)$$

This makes the iron catalyst ideal for use with a hydrogen lean synthesis gas produced from coal gasification. Potassium has long been used as a promoter for iron catalysts. It provides an increase in the alkene yield and a decrease in the CH_4 selectivity [1–3]. Potassium can also increase the catalytic activity for FTS and water–gas shift (WGS) reactions [3–9]. Pretreatment of iron catalysts can have important influences on the FTS activity and selectivity [10–13].

Although CO is believed to be the best activation gas for iron catalysts during catalyst screening studies, hydrogen and/or syngas is utilized in industry due to the process feasibility. Iron catalysts promoted with Mn [14–19], Zn [20,21], group I alkali and group II alkali earth are discussed elsewhere [22,23].

Palladium is widely used in hydrogenation, hydrocracking, hydroisomerization, CO and methane oxidation [24–26], and water–gas shift catalysts formulations [27]. Palladium promotion of cobalt catalysts is reported to enhance the production of iso-paraffins in the FTS reaction [28,29] and for hydroprocessing of coal liquefaction derived aromatics [30]. Palladium is of great interest because of the high solubility of H_2 in the metal surface [31–34]. In a CO oxidation reaction, both CO and oxygen adsorbed on the Pd surface only when CO covers less than one-third of the metal surface [24]. As CO coverage increases to over one-third of the surface, oxygen adsorption is blocked. Li and coworkers studied the FTS over a three-component (Co/Pd/ZHM-5) catalyst and they claimed that Pd enhanced the iso-paraffin selectivity due to the role of Pd as a porthole for H_2 spillover to the zeolite [28].

Richter and Baerns [35] examined Rh and Pd promoted FeMn catalysts and found that Rh and Pd increases activity, decreases olefin fraction and leads to low molecular weight hydrocarbons. CO dissociated to a greater extent on Rh than on Pd. On the other hand, Guan [36] found that promotion of FeMn catalysts with Pd only altered the conversion, which was higher for the Pd promoted catalyst.

The purpose of this study is to investigate the effect of Pd on the FTS selectivity, FTS activity and kinetics as well as on the water–gas shift activity of an iron catalyst. In this study, two palladium promoted catalysts were prepared using a base Fe100/Si5.1 (atomic ratio) material. Results of FTS over Pd promoted iron catalysts were compared to those catalyzed by a K/Fe/Si base catalyst and a Cu/K/Fe/Si catalyst. A range of

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* To whom correspondence should be addressed.
E-mail: davis@caer.uky.edu

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conversions were obtained by varying the syngas space velocities. The results from palladium promoted catalysts were then compared to a Cu-promoted and an iron base catalyst.

2. Experimental

2.1. *Preparation of catalyst*

The precipitated iron base catalyst was prepared using a ferric nitrate solution obtained by dissolving $Fe(NO_3)_3 \cdot 9H_2O$ in distilled and deionized water, and then the amount of tetraethylorthosilicate was added to provide the desired Fe/Si ratio. The mixture was stirred vigorously until the tetraethylorthosilicate had hydrolyzed. A flow of the tetraethylorthosilicate and iron nitrate mixture was added to a CSTR precipitation vessel together with a stream of 30% ammonium hydroxide that was added at a rate to maintain a pH of 9.0. By maintaining the slurry pH at 9 and an average residence time of 6 min, a base catalyst material containing iron and silicon was obtained. The slurry from the CSTR was filtered with a vacuum drum filter and washed twice with deionized water. The final filter cake was dried for 24 h in an oven at 110 °C with flowing air. The dried catalyst was calcined at 350 °C in an air flow for 4 h. For this study, the Fe/Si catalyst base powder was impregnated with the proper amount of aqueous K_2CO_3 solution to produced the desired composition of Fe/Si/K = 100:5.1:1.25 atomic ratio. The catalyst was dried at 110 °C overnight with good mixing following impregnation. A palladium ($Pd(NO_3)_2 \cdot 2H_2O$ in 10% HCl) or copper (cupric nitrate) solution was then added to the base catalyst by incipient impregnation to obtain two palladium promoted and one copper promoted iron catalysts with the compositions shown in table 1.

Table 1
Composition of the catalysts (atomic ratio)

Catalyst ID	Fe	Si	K	Cu	Pd
No Cu/Pd	100	5.1	1.25	0	0
Cu 2.0/Fe100	100	5.1	1.25	2.0	0
Pd 0.002/Fe100	100	5.1	1.25	0	0.002
Pd 0.005/Fe100	100	5.1	1.25	0	0.005

2.2. In situ *activation of catalysts*

In this study, the iron catalyst batches were pretreated in the melted startup wax with H_2 at 220 °C for 24 h. H_2 activation was conducted at atmospheric pressure and the reduction of Fe_2O_3 with H_2 occurs in two steps:

$$3Fe_2O_3 + H_2 \rightarrow 2Fe_3O_4 + H_2O \quad (3)$$

$$Fe_3O_4 + 4H_2 \rightarrow 3Fe + 4H_2O \quad (4)$$

2.3. *Reactor system*

A one-liter continuous stirred tank reactor (CSTR) was used in this study. A sintered metal filter was installed to allow removal of wax samples from the catalyst slurry. The wax sample was extracted through the internal filter and collected in a hot trap held at 200 °C. A warm trap (100 °C) and cold trap (0 °C) were used to collect light wax and the water plus oil samples, respectively, by condensing them from the vapor phase that was continuously withdrawn from the reactor vapor space.

CO and H_2 mass flow controllers were used to provide a simulated synthesis gas of the desired composition. After the catalyst was activated, syngas was introduced at a rate of 10 nL/h/g-Fe. Reaction conditions were 270 °C, 1.3 MPa, $H_2/CO = 0.7$, and a stirrer speed of 750 rpm.

2.4. *Product sampling and analysis*

Daily gas, water, oil, light and heavy wax samples were collected and analyzed using several g.c.'s as described earlier [8,9,11]. A heavy wax sample was collected from the 200 °C hot trap connected to the filter. The vapor phase in the region above the slurry passed continuously to the warm (100 °C) and the cold (0°C) traps located outside the reactor. The light wax and water mixture was collected daily from the warm trap and an oil plus water sample from the cold trap. Tail gas from the cold trap was analyzed with an online HP Quad Series Micro GC, providing molar compositions of C_1—C_7 olefins and paraffins as well as for H_2, CO and CO_2. Hydrogen and carbon monoxide conversions were calculated based on the gas product GC analytical results and the gas flow measured at the reactor outlet. Hydrogen, carbon monoxide and syngas conversion were obtained using the following formula (N = moles of gas):

$$\text{Conversion} = 100\% \times (N_{in} - N_{out})/N_{in} \quad (5)$$

The oil and light wax samples were mixed before analysis with an Agilent 6890 Series GC. The heavy wax was analyzed with an HP5890 Series II Plus GC while the water sample was analyzed using an HP5890 Series II GC.

Runs have been made using stirrer speeds between 200 and 1200 rpm. Above about 400 rpm, the CO conversion was constant; thus, 750 rpm was chosen as a compromise to limit stirrer wear.

3. Results and discussion

3.1. *FTS activity*

All FTS reactions were started at 270 °C, 1.3 MPa and 10 nL/h/g-Fe and the feed syngas space velocity was maintained until a stable CO conversion was obtained at about 72 h of time on stream. Table 2 shows the results of

Table 2
Summary of the Fischer–Tropsch synthesis data for the four catalysts (270 °C, 1.3 MPa and 10 nL/h/g-Fe)

Catalyst	K1.25/Si5.1/ Fe100	Pd 0.005/K1.25/ Si 5.1/Fe100	Pd 0.002/K1.25/ Si 5.1/Fe100	Cu 2.0/K1.25/ Si5.1/Fe100
CO conversion (%)	46.4	73.7	65.7	65.6
H_2 conversion (%)	43.0	65.5	61.3	53.9
Syngas conversion (%)	45.0	70.3	63.9	60.8
Methane selectivity (%)	8.80	10.2	9.05	10.6
CO_2 selectivity (%)	45.1	46.8	42.5	47.3
Hydrocarbon rate (g/h/g-Fe)	0.96	1.48	1.30	1.43
Olefin/paraffin ratio				
C_2	0.92	0.27	0.39	0.49
C_3	4.40	3.03	3.47	3.61
C_4	3.30	1.08	1.56	2.96
C_5	2.80	0.83	1.19	1.92
water–gas shift quotient $\frac{P_{CO_2}P_{H_2}}{P_{H_2O}P_{CO}}$	8.67	24.3	17.3	9.28

FTS at the stabilized CO conversion conditions. Without Cu or Pd, the base iron catalyst provided 45% syngas conversion. Palladium promotion enhanced the syngas conversion to 66% and 74% for the 0.002 and 0.005 Pd catalysts, respectively. Copper promotion led to 66% CO conversion. Thus, the higher loading of Pd had better promoting properties on the FTS activity than 2% copper while the lower Pd loading (0.002%) was as active as the Cu promoted catalyst.

A catalyst with 1.25K:100Fe is a low alpha catalyst (ca. 0.70–0.75) and will therefore produce low molecular weight FTS products. The alpha values for similar catalysts have been well documented at steady-state conditions in our earlier work and are in the range of 0.70–0.75. Since the space velocities were changed frequently the product distribution is given for the products collected early in the run prior to space velocity changes.

After the FTS reaction, conversion was stable at about 72 h of time-on-stream, feed gas flow rate was then varied to obtain conversions at different space velocities, and figure 1 show these conversions. Pd promotion always produces the highest syngas conversion while the base catalyst has the lowest conversion at all space velocities. An approximate 10% enhancement of the syngas conversion was obtained with copper promotion, and additional 10% increase for the higher level of Pd promotion.

The data in table 2 also show that Pd can produce 40–50% higher hydrocarbon productivity than the base catalyst while Cu promotion increases the hydrocarbon rate by 30% at 270 °C, 1.3 MPa and 10 nL/h/g-Fe. Figure 2 shows the results of hydrocarbon rate as the function of syngas conversion. The base catalyst and the copper promoted catalyst showed a nearly linear decline in hydrocarbon production with increasing syngas conversion, and Pd promoted catalyst produced a stable hydrocarbon rate of 1.4 g/h/g-Fe. At a syngas conversion lower than 55%, copper produced a higher hydrocarbon rate than Pd promotion; this was due to the high WGS activity for the Pd promoted catalyst.

3.2. Selectivity

CH_4 selectivity was slightly higher for the Cu or Pd promoted catalysts compared to the base iron catalyst. All promoted catalysts produced 9–10% CH_4 selectivity.

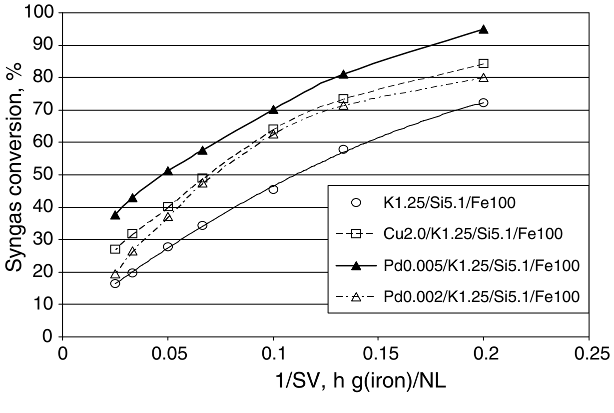

Figure 1. Syngas conversion versus space time for the four catalysts (270 °C; 1.3 MPa and 10 nL/h/g-Fe).

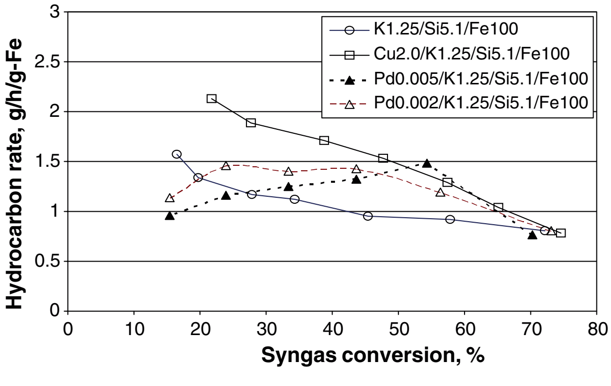

Figure 2. Hydrocarbon rate versus syngas conversion (270 °C; 1.3 MPa and 10 nL/h/g-Fe).

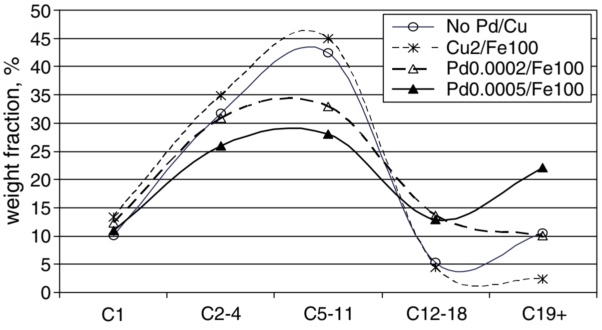

Figure 3. Hydrocarbon distribution (270 °C; 1.3 MPa and 10 nL/h/g-Fe).

The data in table 2 indicate that Pd promotion significantly decreases the olefin to paraffin ratio due to its hydrogenation property while Cu produced an olefin to paraffin ratio between the base catalyst and the Pd promoted catalysts.

Hydrocarbon distributions are shown in figure 3. As described above, C_1 yield was at about the same level for all the catalysts used in this study. Pd promoted catalysts produced lower gaseous (C_2—C_4) but higher diesel (C_{12}—C_{18}) fractions than the base and Cu promoted catalysts. Without Cu or Pd, the base catalyst produced 47% of gasoline (C_5—C_{11}) fraction while the Pd 0.005/Fe100 catalyst generated less than 30%. The Pd promoted catalyst produced a higher amount of long-chain (C_{19+}) hydrocarbons (22%) than the base catalyst (3%).

Isomer products (branched products/total products for each carbon number) were not enhanced by adding Pd, as suggested by Li [28], since the Pd promoted catalyst yielded an isomer selectivity that was similar to the base catalyst (figure 4).

3.3. *Water–gas shift*

The water–gas shift reaction produces carbon dioxide, as expressed in equation (2). Figure 5 shows the water–gas shift quotient, given by the following equation, as a function of syngas conversion.

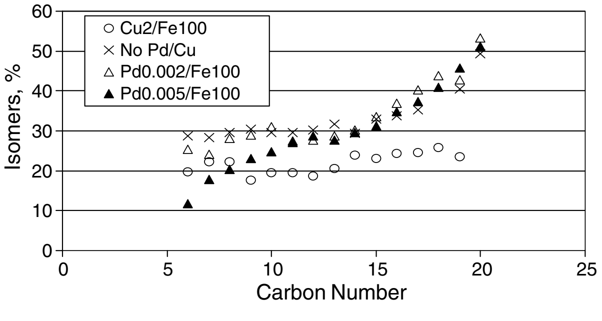

Figure 4. Effect of promoters on isomer content (270 °C; 1.3 MPa and 10 nL/h/g-Fe).

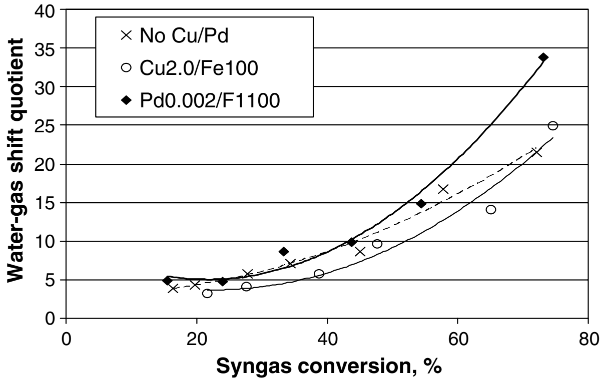

Figure 5. water–gas shift quotient versus syngas conversion for the four catalysts.

$$Q_{WGS} = \frac{P_{CO_2}P_{H_2}}{P_{CO}P_{H_2O}} \tag{6}$$

This quotient is frequently used even though it changes slowly at lower conversions; thus, figure 5 should be considered together with the data shown in figure 2.

Because of the low H_2/CO ratio of the coal derived syngas, the changes in the water–gas shift reaction quotient is not as significant at low syngas conversions as at high conversions. As the conversion increase, H_2 becomes insufficient and water–gas shift provides part of the H_2 for the FTS reaction. Thus, water–gas shift becomes more critical at high conversions than at low conversions. Figure 5 shows that at low and intermediate syngas conversion, Pd produced a similar water–gas shift quotient as the base catalyst and the Cu promoted catalyst. At a conversion higher than 55%, however, the Pd promoted catalyst generated a higher water–gas shift quotient than the other two catalysts. The dominant role of the reactant concentrations (P_{H_2} and P_{CO}) on Q at low CO conversions is largely responsible for the four catalysts having similar Q's at lower CO conversions.

Under normal FTS condition, the Bouduard reaction is negligible:

$$2CO \rightarrow C + CO_2 \tag{7}$$

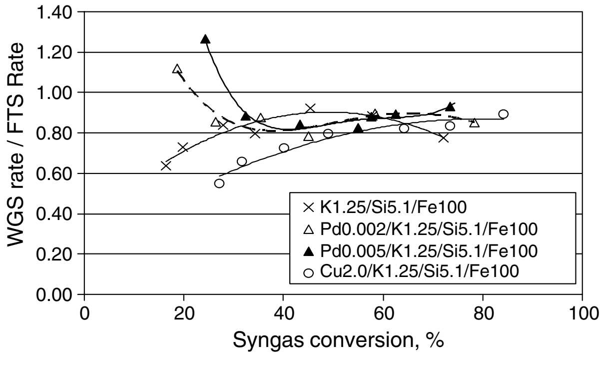

Figure 6. Ratio of WGS rate/FTS rate with increasing syngas conversion.

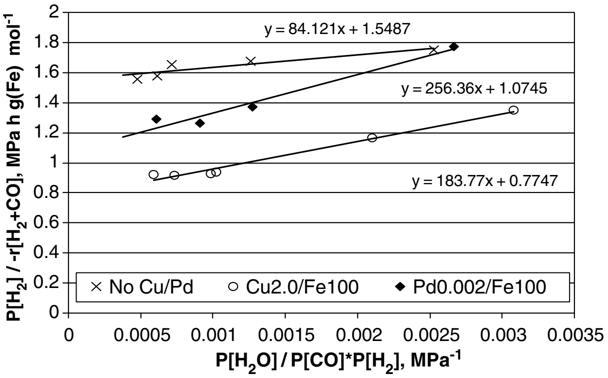

Figure 7. Kinetic plot to obtain rate constant, k, and adsorption coefficient b.

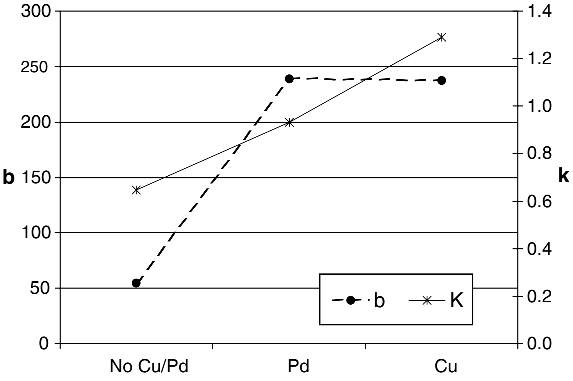

Figure 8. Effect of promoter on FTS kinetic parameters.

Then the water–gas shift rate is to the rate of carbon dioxide formation. Thus the Fischer–Tropsch rate can be expressed as:

$$r_{FT} = r_{CO} - r_{CO_2} \tag{8}$$

and the WGS rate as

$$r_{WGS} = r_{CO_2} \tag{9}$$

The ratios of water–gas shift to FTS rates for the four catalysts are shown in figure 6. In all cases, the rate of water–gas shift is lower than the rate of FTS at a syngas conversion higher than 30%. The base and Cu promoted catalysts exhibited an increasing water–gas shift to FTS rate ratio with increasing syngas conversion. A higher ratio of water–gas shift to FTS rate was observed at a syngas conversion of 20–30% for Pd0.005/Fe100 and Pd0.005/Fe100 catalysts, but more detailed studies would be required to validate that this is actually the case.

3.4. Kinetics

The kinetics of FTS reaction was discussed in detail by van Der Lann and Beenackers [37]. Huff and Satterfield [38] proposed a FTS reaction rate as follows:

$$-r_{syngas} = \frac{kP_{CO}P_{H_2}^2}{P_{CO}P_{H_2} + bP_{H_2O}} \tag{10}$$

Thus, changes in catalyst FTS activity could be due to changes in the rate constant (k) or to CO, H_2 and water partial pressures. In addition, the rate and extent of the WGS reaction has a major effect on the FTS activity when iron catalyst was used for a low H_2/CO ratio syngas feed.

To obtain the kinetic parameters k and b, the reaction rate expression given in equation (10) was then rearranged as

$$\frac{P_{H_2}}{-r_{syngas}} = \frac{1}{k} + \frac{bP_{H_2}}{kP_{CO}P_{H_2O}} \tag{11}$$

A plot of the date using equation (11) yields a line with a slope of b/k and intercept of $1/k$, as shown in figure 7. The reaction constant, k, increases in the order of base catalyst, Pd and Cu promoted catalysts while the adsorption parameter b is approximately equal for the Pd and Cu promoted catalysts, and the promoted catalysts are higher than the unpromoted catalyst. These results indicate that both Cu and Pd enhance the activity of iron catalyst, which is consistent with the results give in table 2 & figure 8.

4. Conclusions

A series of studies were conducted to investigate the effect of Pd on the FTS selectivity, activity and kinetics as well as on the water–gas shift activity of an iron catalyst. In this study, two palladium promoted catalysts were prepared from the base Fe100/Si5.1(atomic ratio) catalyst. Results of FTS for two palladium promoted catalysts were compared to those catalyzed by the K/Fe/Si base catalyst and the Cu/K/Fe/Si catalyst.

This study indicates that even very low levels of Pd significantly enhanced the FTS activity. Palladium promotion generated the highest syngas conversion while CH_4 changed little, compared to the results for the base catalyst and the Cu promoted catalysts. A higher hydrocarbon rate was also observed for the Pd promoted catalyst than for the base catalyst. Palladium promoted catalysts produced less gas and gasoline fractions and more diesel and heavy products. Although Cu promotion lowered the iso-hydrocarbon products, Pd promotion led to similar isomer production when compared to iron base catalyst. Palladium promotion led to a negative effect on C_2—C_4 olefin to paraffin ratio.

At low and intermediate syngas conversions, Pd promoted catalysts produced water–gas quotients that were similar to the Cu and base catalysts. At high syngas conversions, Pd had a higher WGS quotient than the other catalysts.

Kinetic data were obtained by varying the syngas feed space velocities over a range from 5 to 40 nL/h/g-Fe. A rate expression [38] was used to get the two parameters: rate constant, k, and an absorption parameter, b. The rate constant for the Pd promoted catalyst for FTS is higher than the base catalyst but lower than Cu promoted catalyst. A similar adsorption parameter is obtained for the Pd promoted catalyst and the Cu promoted catalyst, and both are higher than for the base catalyst.

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