

Technology Development for Iron and Cobalt Fischer-Tropsch Catalysts

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Abstract

CAER

Fischer-Tropsch synthesis was studied using precipitated iron catalysts with a syngas typical of that obtained from natural gas. The amount of potassium promoter and the reaction conditions (pressure, temperature, gHSV and H₂/CO ratio) were changed to optimize the catalyst efficiency. Twenty-one cobalt catalysts have been prepared to study the effects of preparation method, pretreatment conditions, support material, particle size and cobalt loading on FTS activity. A comparison study was made of FTS for an unpromoted cobalt catalyst in a conventional fixed bed, a CSTR and a supercritical reactor.

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The structure, reduction and carburization behavior, and catalytic properties of Fischer-Tropsch synthesis (FTS) catalysts based on Fe-Cu-K oxides were studied using transient reaction methods and *in-situ* X-ray absorption spectroscopy. Mass spectrometric analysis of initial FTS products detected initial carburization and reduction of Fe₂O₃ precursors and a concurrent increase in FTS rates. Steady-state rates, however, were obtained after removal of only about 10 % of the O-atoms in Fe₂O₃, suggesting that only near-surface carbide layers are required to form FTS active sites. Cu not only increases the reduction and carburization of Fe₂O₃ precursors, but it also appears to promote FTS reactions. The addition of K to Fe-Cu oxide also increases the reduction/carburization as well as FTS reaction rates. *In-situ* Fe K-edge X-ray absorption studies confirmed that only incipient conversion of Fe₂O₃ to Fe₃O₄ and Fe_xC is required to obtain steady-state FTS reaction rates. The extent of carburization increases with time on stream without a detectable increase in the FTS reaction rates. A remaining Fe₃O₄ core and its progressive carburization apparently does not influence the catalytic properties of Fe carbides. K and Cu both

increase the carbide formation rates, and the combination of K and Cu has stronger effects on the carburization of Fe oxides than the additive effects of each separate component. A contracting sphere nucleation-growth model is consistent with the reduction and carburization behavior and with the observed effects of Cu and K on FTS reactions. The kinetic study of Co-based catalysts has continued with the analysis of previously obtained data, but the experimental component was briefly interrupted during this reporting period because of a transition in post-doctoral staffing within the project.

Executive Summary

CAER

Fischer-Tropsch synthesis was studied using precipitated iron catalysts with syngas typical of that obtained from natural gas. The amount of potassium promoter and the reaction conditions were changed to optimize the catalyst efficiency.

Potassium had little impact on FT activity but did effect selectivity and in particular the water-gas shift reaction. Potassium increased the water-gas shift rate relative to the FT rate and as a consequence decreased the H₂/CO usage ratio. Pressure and temperature can have significant effects on the activity and selectivity of iron based FT catalysts using syngas similar to that obtained from natural gas. By simultaneously decreasing temperature and increasing pressure it was possible to increase the H₂/CO usage ratio while also maintaining reasonable FT activity. Only the catalyst with atomic composition 100Fe/4.6Si/2.0Cu/1.44K was able to maintain a H₂/CO usage ratio similar to the H₂/CO syngas feed ratios. In general, the water-gas shift activity of the 100Fe/4.6Si/2.0Cu/3.0K and 100Fe/4.6Si/2.0Cu/5.0K catalysts was too high.

A study was made to examine the conditions under which product diffusion limitation might exist in catalyst pores. The FT reaction is simulated in a CSTR reactor whose modeling and simulation was previously reported in the last quarterly report.

Due to the effect of VLE in the Fischer-Tropsch reactor, the relative concentration of a hydrocarbon product in the catalyst pores decreases with increasing carbon number until about C₂₀ under steady state. The impact of internal diffusion of a product is significant only when there is internal diffusion limitation of reactants, and this significance decreases with increasing carbon number. Therefore, it can be deduced that the two alpha product distribution in FT reactions is not due to the effect of product diffusion limitation, even if it exists under some reaction conditions.

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In this reporting period, a switch method has been developed in order to investigate the initial reduction and carburization behavior of Fe oxides and effects of K and Cu on the reactivity of Fe oxides in FTS. In this method, the samples were pretreated in dry air up to 673 K and cooled down to 523 K in He. The flowing He stream was rapidly switched to a mixture gas of synthesis gas and Ar ($H_2/CO=2$). The resulting isothermal transients were monitored as a function of time at 523 K by on-line mass spectrometry. We have almost completed our *in-situ* X-ray absorption spectroscopic (XAS) studies at the Stanford Synchrotron Radiation Laboratory (SSRL) with emphasis on Fe K-edge measurements of the initial phase evolution during the reduction and carburization of Fe oxides. A combination of these two techniques allows a study of the structure-function rules by monitoring the evolution of FTS activity and the phase changes of Fe-K-Cu oxides at synthesis conditions as FTS reactions occur.

We have measured isothermal transients using Fe_2O_3 , Fe_2O_3 -Cu, Fe_xC -Cu, Fe_3O_4 -Cu, Fe_2O_3 -K, Fe_2O_3 -K-Cu during reduction/carburization and during subsequent FTS in synthesis gas at 523 K ($H_2/CO=2$). Concurrently, we have monitored the structural evolution of these compounds during the initial reduction and carburization using *in-situ* X-ray absorption techniques. The principal objective is to identify the active phases and site requirements for the FTS reaction and to maximize the density of required synthesis through additives and novel synthesis protocols. In addition, we explored the effects of K and Cu on the initial reduction and carburization behavior of these compounds in synthesis gas. The results showed that neither Fe_2O_3 nor O-deficient Fe_2O_{3-x} are active phases for FTS reactions. Only near-surface carbide layers are required to form FTS active sites, the catalytic activity of Fe carbides is not influenced by the presence of Fe oxide cores or by its progressive carburization to Fe_xC . Cu not only

shortens the induction period for the reduction and carburization of Fe_2O_3 by dissociating H_2 , but also increases FTS rates, possibly by leading to the formation of higher surface carbide crystallites; K assists CO dissociation and it significantly increases FTS rates. An appropriate combination of Cu and K provides the adsorbed hydrogen and carbon ratio required for maximum $-\text{CH}_2-$ monomer concentrations and highest C_{5+} synthesis rates. A contracting sphere nucleation-growth model has been proposed to describe the effects of Cu and K on the reduction and carburization behavior of these oxides or carbides in synthesis gas.

The kinetic study of Co-based catalysts has continued with the analysis of previously obtained data, but the experimental component was briefly interrupted during this reporting period because of a transition in post-doctoral staffing and modification to the two microreactors. Work continues on an efficient code to evaluate the suitability of specific mechanism-based rate expression to describe the complex experimental dependence of FTS rates and selectivities on reactant and product concentrations and the critical role of primary and secondary reactions in catalyst performance.

Task 1. Iron Catalyst Preparation

The objective of this task is to produce robust intermediate- and high- α catalysts.

No scheduled activity to report.

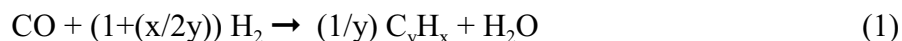
Task 2. Catalyst Testing

The objective of this task is to obtain catalyst performance on the catalysts prepared in Task 1.

Fischer-Tropsch Synthesis with Precipitated Iron Catalysts Using Hydrogen Rich Syngas

Introduction

The two most common sources of syngas proposed for Fischer-Tropsch synthesis are coal and natural gas. The FTS reaction requires a H_2/CO ratio greater than 2:1.



Advanced coal gasifiers produce syngas that is deficient in hydrogen with respect to the FTS stoichiometry (1). Iron based FTS catalysts are capable of utilizing hydrogen lean syngas because they are also active for the water-gas shift reaction. Unconverted CO can react with H_2O generated by the FTS to produce additional H_2 .



The overall effect is a decrease in catalyst efficiency because a significant amount of CO is converted to CO_2 ; however, the need for an external water-gas shift step is eliminated.

Cobalt catalysts have much lower water-gas shift activity than iron catalysts and are generally not suitable for FTS with coal derived syngas without an external water-gas shift step. Syngas derived from natural gas is more hydrogen rich than coal derived syngas and as a consequence is better suited for cobalt catalysts. Using iron based catalysts for the conversion of syngas derived from natural gas is more complicated because the water-gas shift is not needed to

the same extent as with coal derived syngas and will result in lower catalyst efficiency. We have shown that when using hydrogen lean syngas, typical of that derived from coal, it is possible to decrease the water-gas shift rate relative to the FTS rate by operating at low to moderate conversion (30% to 50%) (2,3). At low conversion, the FTS rate is higher than the water-gas shift rate; as the CO conversion is increased, the water-gas shift rate approaches the rate of the FTS (Figure 1). For syngas with $H_2/CO=0.67$, the H_2/CO usage ratio is equal to the H_2/CO ratio of the syngas at conversions between 40 and 70% (H_2 conversion= CO conversion, Figure 1) depending on the type and amount of promoters present. By running a low conversion with H_2/CO usage ratio equal to the H_2/CO ratio of the syngas it is possible to operate with recycle or with multiple reactors in series without having to adjust the syngas composition (4). Using recycle or multiple reactors allows for higher productivity and more efficient use of CO. In the present study we have conducted FTS on precipitated iron catalysts with syngas typical of that obtained from natural gas. The amount of potassium promoter and the reaction conditions (pressure, temperature, gHSV and H_2/CO ratio) were changed to optimize the catalyst efficiency.

Experimental

Catalysts were prepared by continuous precipitation from aqueous $Fe(NO_3)_3 \cdot 9H_2O$ (1.17 M) and concentrated NH_4OH (15.6M) in a continuous stirred tank reactor at pH 9.5. Hydrolyzed tetraethyl orthosilicate was added to the iron(III) nitrate solution to give an atomic ratio of 100Fe/4.6Si. The catalyst slurry was filtered continuously with one or more six inch rotary drum vacuum filters. The resulting catalyst cake was washed and filtered twice with a volume of distilled deionized water equal to the volume of the previous filtrate. A 5 kg catalyst batch was precipitated in this manner, oven dried in flowing air at 110°C and crushed to -325 mesh. The catalyst was calcined in air at 350°C for 4 hours. The 100Fe/4.6Si precursor was impregnated

with aqueous $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and dried at 110°C to give an atomic composition of 100Fe/4.6Si/2.0Cu. The catalyst was then impregnated with aqueous KNO_3 to give atomic compositions of 100Fe/4.6Si/2.0Cu/1.44K, 100Fe/4.6Si/2.0Cu/3.0K and 100Fe/4.6Si/2.0Cu/5.0K.

All FTS runs were conducted in a one liter autoclave operated as a continuous stirred tank reactor (CSTR). Each catalyst (5 g) was suspended in 310 g of Ethylflo 164 hydrocarbon oil (Ethyl Corporation) which is a 1-decene trimer. H_2 and CO flow rates were controlled by two mass flow controllers (Brooks Instruments) with the resulting synthesis gas composition regulated by adjusting the flow rate of the appropriate gas. The synthesis gas, after passing through a 2 L mixing vessel, was delivered to the catalyst slurry through a dip tube that extended to below the impeller blade. The reactor effluent exited the reactor and passed sequentially through two traps maintained at 60°C and 0°C . Accumulated reactor wax was removed daily through a tube fitted with a porous metal filter ($0.5 \mu\text{m}$). Uncondensed effluent was directed to an on-line Hewlett Packard 4 channel Quad Series Micro GC for determination of CO, H_2 , CO_2 , CH_4 and $\text{C}_2\text{-C}_8$ alkanes and alkenes. Liquid samples were analyzed with a Hewlett-Packard 5890 GC equipped with a 60 m DB-5 capillary column.

All catalysts were activated with CO. CO flow (25 slph) was started at ambient temperature and 1.3 MPa and the temperature was increased to 270°C at 2°C min^{-1} . After reaching the activation temperature, the conditions were maintained for 24 h. Initial FTS conditions were 270°C , 1.3 MPa, $\text{H}_2/\text{CO}=1.7$ and $\text{ghsv}=40 \text{ sl h}^{-1} \text{ g-Fe}^{-1}$. Temperature, pressure, ghsv and H_2/CO feed ratio were changed periodically as outlined in Table 1.

Table 1					
FTS Conditions					
Condition	Time (h)	Temperature (°C)	Pressure (MPa)	ghsv (sl h ⁻¹ g-Fe ⁻¹)	H ₂ /CO
1	0-24	270	1.3	40	1.7
2	24-48	270	1.3	65	1.7
3	48-120	250	1.3	22	1.7
4	120-144	250	2.5	22	1.7
5	144-168	230	2.5	22	1.7
6	168-286	230	3.2	22	1.7
7	286-310	230	3.2	22	1.4
8	310-332	230	3.2	22	2.0

Results

Condition 1, 270°C, 1.3 MPa, H₂/CO=1.7, ghsv=40 sl h⁻¹ g-Fe⁻¹.

Syngas conversion data for the three runs are shown in Figure 2. Under the initial conditions, the syngas conversion ranged between 41 and 46% for the three catalysts which is indistinguishable within the expected experimental error. Hydrocarbon rates (Figure 3) were between 3.4 and 3.8 g h⁻¹ g-Fe⁻¹. Methane selectivity (Figure 4) decreased with increasing potassium loading from 11 to 7 to 5% (carbon converted to hydrocarbon) for the 1.44K, 3.0K and 5.0K loadings, respectively. The H₂/CO usage ratio increased with decreasing potassium loading; however, all were much lower than the H₂/CO feed ratio of 1.7 (Figure 5).

Condition 2, 270°C, 1.3 MPa, H₂/CO=1.7, ghsv=65 sl h⁻¹ g-Fe⁻¹.

In order to suppress the water-gas shift rate relative to the FTS rate and subsequently increase the H₂/CO usage ratio, the ghsv was increased from 40 to 65 sl h⁻¹ g-Fe⁻¹ for each catalyst. Increasing the ghsv caused the syngas conversion to decrease to 33%, 34% and 26%

and the methane selectivity to decrease to 10%, 5.3% and 4.0% for the 1.44K, 3.0K and 5.0K catalysts, respectively. In addition, hydrocarbon rate increased for all catalysts. The ratio of water gas shift rate (rate of CO₂ production) to FT rate (rate of CO converted less CO₂) decreased (Figure 6); however, the H₂/CO usage did not increase significantly for any of the catalysts.

Condition 3, 250°C, 1.3 MPa, H₂/CO=1.7, gHSV=22 sl h⁻¹ g-Fe⁻¹.

The temperature was lowered to 250°C and the gHSV was simultaneously lowered to 22 sl h⁻¹ g-Fe⁻¹ to maintain reasonable conversion. The syngas conversion increased slightly for each catalyst to 35%-39%. The ratio of water-gas shift rate to FT rate decreased (Figure 6) and the H₂/CO usage ratio increased for all catalysts (Figure 5). Hydrocarbon production rate decreased substantially from 4.6, 4.6 and 4.0 g h⁻¹ g-Fe⁻¹ to 1.75, 1.75 and 1.62 g h⁻¹ g-Fe⁻¹ for the 1.44K, 3.0K and 5.0K catalysts, respectively. Methane selectivity also decreased for each catalyst.

Condition 4, 250°C, 2.5 MPa, H₂/CO=1.7, gHSV=22 sl h⁻¹ g-Fe⁻¹.

The pressure was increased to 2.5 MPa and all other conditions were maintained the same. Syngas conversion (50 to 53%) and hydrocarbon productivity (2.26, 2.41 and 2.48 g h⁻¹ g-Fe⁻¹ for 1.44K, 3.0K and 5.0K, respectively) increased for each catalyst. Methane selectivity decreased for the 1.44K and 3.0K catalysts but increased for the 5.0K catalyst (Figure 4). The H₂/CO usage ratio increased for all three catalysts; however, they remained well below the H₂/CO feed ratio of 1.7 (1.19, 1.44K; 0.99, 3.0K; 0.89, 5.0K).

Condition 5, 230°C, 2.5 MPa, H₂/CO=1.7, gHSV=22 sl h⁻¹ g-Fe⁻¹.

Temperature was decreased to 230°C and all other reaction conditions were held constant. Syngas conversion and hydrocarbon production rate decreased for each catalyst; however, the largest drop was for the 5.0K catalyst (Figures 2-3). Methane selectivity decreased from 8.0% to 4.1% for the 1.44K catalyst, from 4.0% to 2.2% for the 3.0K catalyst and from 4.6% to 2.3% for

the 5.0K catalyst. The relative water-gas shift rate decreased substantially for each catalyst and correspondingly the H₂/CO usage ratio increased to 1.46 (1.44K), 1.24 (3.0K) and 1.12 (5.0K).

Condition 6, 230°C, 3.2 MPa, H₂/CO=1.7, gHSV=22 sl h⁻¹ g-Fe⁻¹.

Increasing the pressure from 2.5 MPa to 3.2 MPa caused the syngas conversion and hydrocarbon production rate to decrease. Methane selectivity was not effected significantly for any K loading as was the case for the H₂/CO usage ratio.

Condition 7, 230°C, 3.2 MPa, H₂/CO=1.4, gHSV=22 sl h⁻¹ g-Fe⁻¹.

The H₂/CO feed ratio was decreased to 1.4. There was no appreciable effect on the syngas conversion or the hydrocarbon production rate. The H₂/CO usage ratio closely approached the feed ratio for the 1.44K catalyst (1.33); however, it was lower for the 3.0K (1.17) and 5.0K (1.09) catalysts. Methane selectivity decreased for each catalyst (Figure 4).

Condition 8, 230°C, 3.2 MPa, H₂/CO=2.0, gHSV=22 sl h⁻¹ g-Fe⁻¹.

Increasing the H₂/CO feed ratio to 2.0 had no effect on the syngas conversion or the hydrocarbon production rate as compared to the same conditions with H₂/CO feed ratio of 1.7. Methane selectivity increased with the increase in H₂/CO feed ratio. The H₂/CO usage ratio increased for each catalyst but was lower than the feed ratio (Figure 5).

Discussion

There was little difference in the FT activity of the 1.44K and 3.0K catalysts; however, the 5.0K catalyst had slightly lower syngas conversion and hydrocarbon production rate under most of the conditions studied. Increasing potassium decreased methane selectivity (Figure 4), increased the water-gas shift reaction rate relative to the FT rate (Figure 6) and decreased the H₂/CO usage ratio (Figure 5).

In an effort to make the H₂/CO usage ratio equivalent to the H₂/CO ratio of the syngas, reaction pressure, temperature and gHSV were varied. Increasing the gHSV (Condition 2) decreased the syngas conversion and increased the hydrocarbon production rate. The decrease in conversion caused the methane selectivity and relative water-gas shift reaction to decrease. Increasing the gHSV had little impact on the H₂/CO usage ratio. Increasing the reaction pressure (Conditions 4 and 6) had mixed results for the FT activity and product. When the pressure was increased from 1.3 MPa to 2.5 MPa at 250°C (Condition 4) the syngas conversion and hydrocarbon productivity rate increased sharply for each catalyst. Despite the increase in conversion, methane selectivity decreased, the water-gas shift rate relative to the FT rate decreased and the H₂/CO usage ratio increased slightly. In contrast, increasing the pressure from 2.5 MPa to 3.2 MPa at 230°C had very little effect on FT activity or selectivity. It is not clear from the current data if there is an optimum pressure or if pressure changes have a different effect at 250°C and 230°C. Reaction temperature also has a large impact on FT activity and selectivity. When the temperature was reduced from 250°C to 230°C (Condition 5) the syngas conversion and hydrocarbon production rate decreased as expected. There was a large decrease in methane selectivity and a substantial increase in H₂/CO usage ratio for all three catalysts.

The impact of changing the H₂/CO ratio of the syngas was also studied. Decreasing the H₂/CO syngas ratio from 1.7 to 1.4 (Condition 7) had no impact on the syngas conversion or the hydrocarbon production rate; however, methane selectivity decreased appreciably for each catalyst. The 1.44K catalyst had a H₂/CO usage ratio of 1.33 while it was somewhat lower for the 3.0K (1.17) and 5.0K (1.09) catalysts. When the H₂/CO syngas ratio was increased to 2.0 (Condition 8) there was no significant change in FT activity and the methane selectivity increased. The H₂/CO usage ratio for each catalyst was below the H₂/CO syngas ratio: 1.54 for

the 1.44K catalyst, 1.32 for the 3.0K catalyst and 1.20 for the 5.0K catalyst. Only the 1.44K catalyst operating at 230°C, 3.2 MPa, $H_2/CO=1.4$ and $ghsv=22 \text{ sl h}^{-1} \text{ g-Fe}^{-1}$ had a H_2/CO usage ratio comparable to the H_2/CO syngas ratio.

Conclusions

Potassium had little impact on FT activity but did effect selectivity and in particular the water-gas shift reaction. Potassium increased the water-gas shift rate relative to the FT rate and as a consequence decreased the H_2/CO usage ratio. Pressure and temperature can have significant effects on the activity and selectivity of iron based FT catalysts using syngas similar to that obtained from natural gas. By simultaneously decreasing temperature and increasing pressure it was possible to increase the H_2/CO usage ratio while also maintaining reasonable FT activity. Only the catalyst with atomic composition 100Fe/4.6Si/2.0Cu/1.44K was able to maintain a H_2/CO usage ratio similar to the H_2/CO syngas ratios. In general, the water-gas shift activity of the 100Fe/4.6Si/2.0Cu/3.0K and 100Fe/4.6Si/2.0Cu/5.0K catalysts was too high.

References

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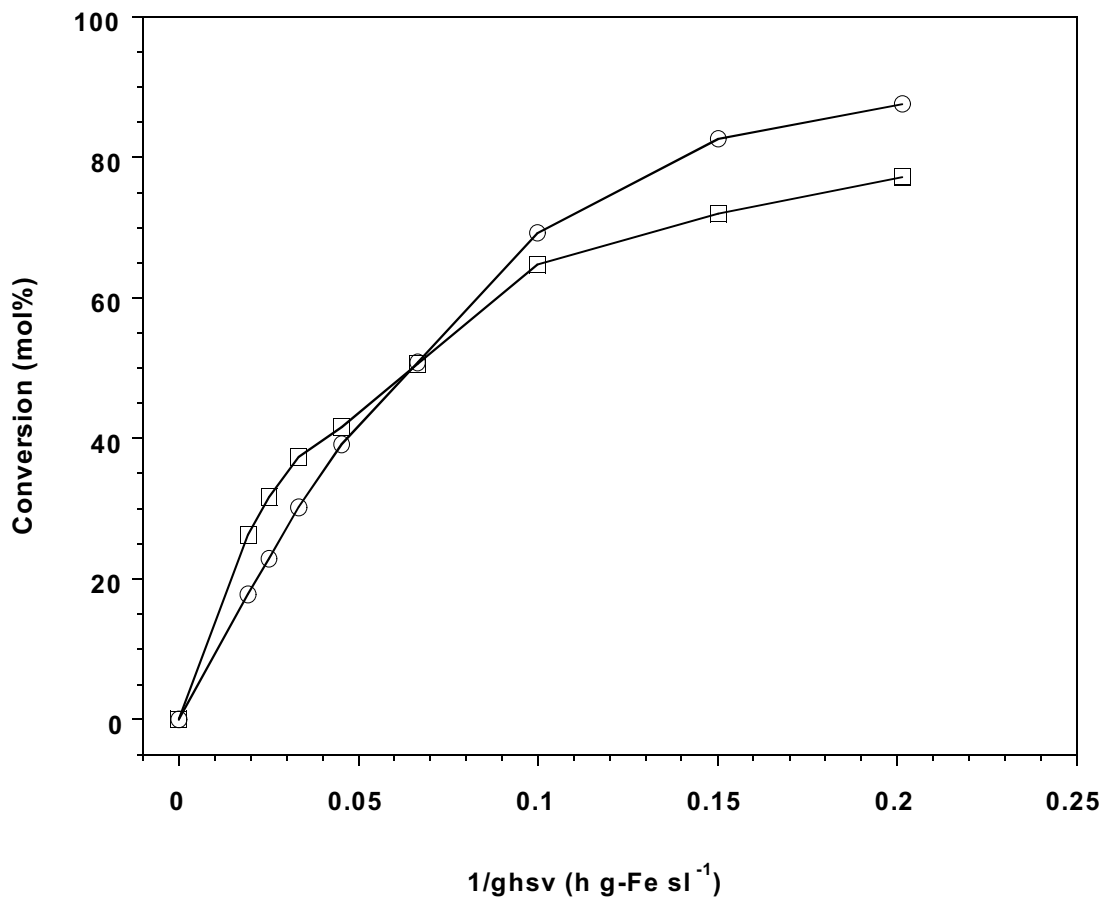


Figure 1. CO and H₂ conversion as a function of reciprocal space velocity for a 100Fe/4.6Si/2.2K catalyst. (○), CO conversion and (□), H₂ conversion.

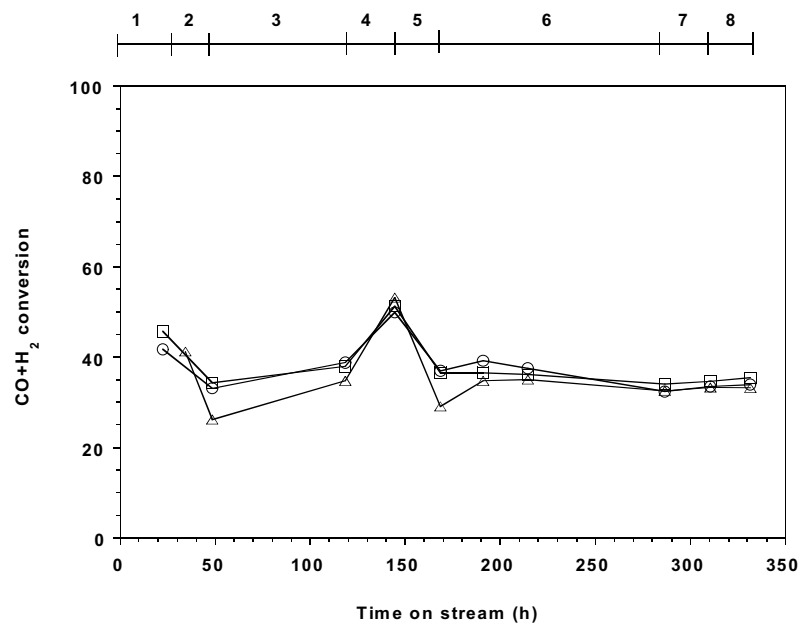


Figure 2. Syngas conversion as a function of time on stream for (○), 100Fe/4.6Si/2.0Cu/1.44K, (□), 100Fe/4.6Si/2.0Cu/3.0K and (△), 100Fe/4.6Si/2.0Cu/5.0K catalysts. Conditions are identified on time line above graph (as defined in Table 1).

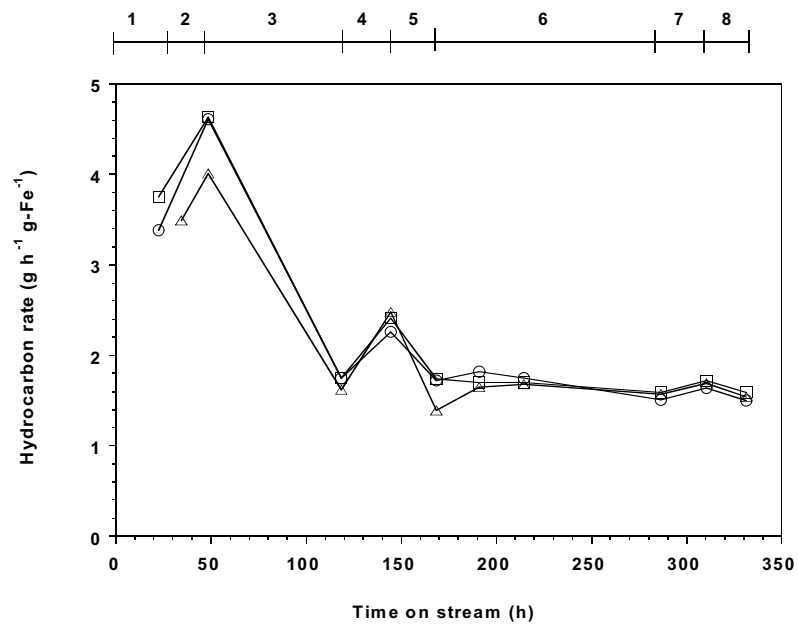


Figure 3. Hydrocarbon production rate as a function of time on stream for (○), 100Fe/4.6Si/2.0Cu/1.44K, (□), 100Fe/4.6Si/2.0Cu/3.0K and (△), 100Fe/4.6Si/2.0Cu/5.0K catalysts. Conditions are identified on time line above graph.

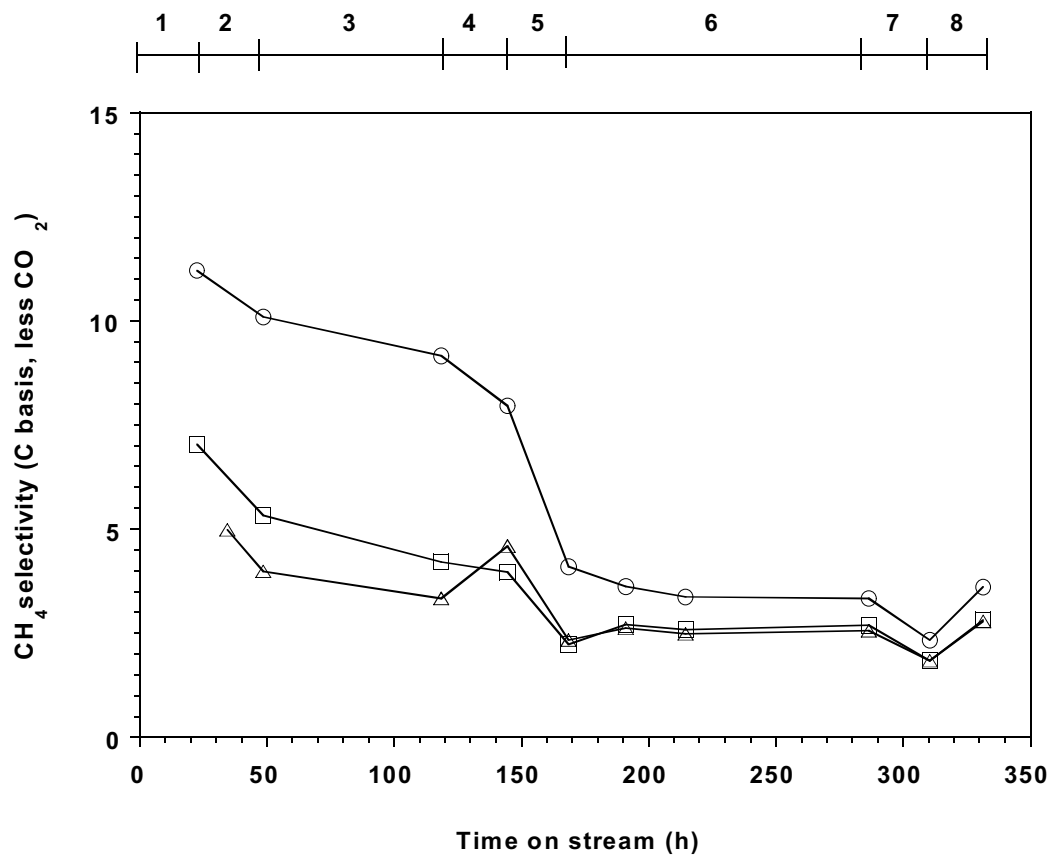


Figure 4. Methane selectivity as a function of time on stream for (○), 100Fe/4.6Si/2.0Cu/1.44K, (□), 100Fe/4.6Si/2.0Cu/3.0K and (△), 100Fe/4.6Si/2.0Cu/5.0K catalysts. Conditions are identified on time line above graph.

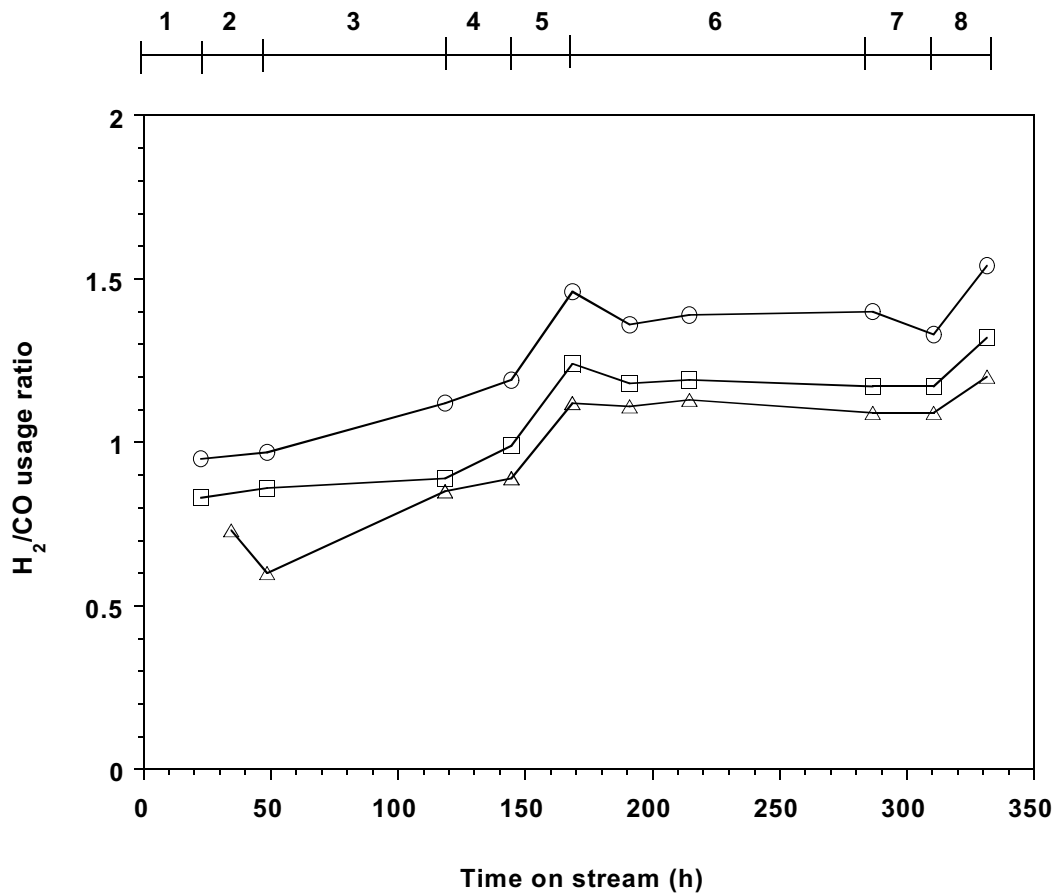


Figure 5. H₂/CO usage ratio as a function of time on stream for (○), 100Fe/4.6Si/2.0Cu/1.44K, (□), 100Fe/4.6Si/2.0Cu/3.0K and (△), 100Fe/4.6Si/2.0Cu/5.0K catalysts. Conditions are identified on time line above graph.

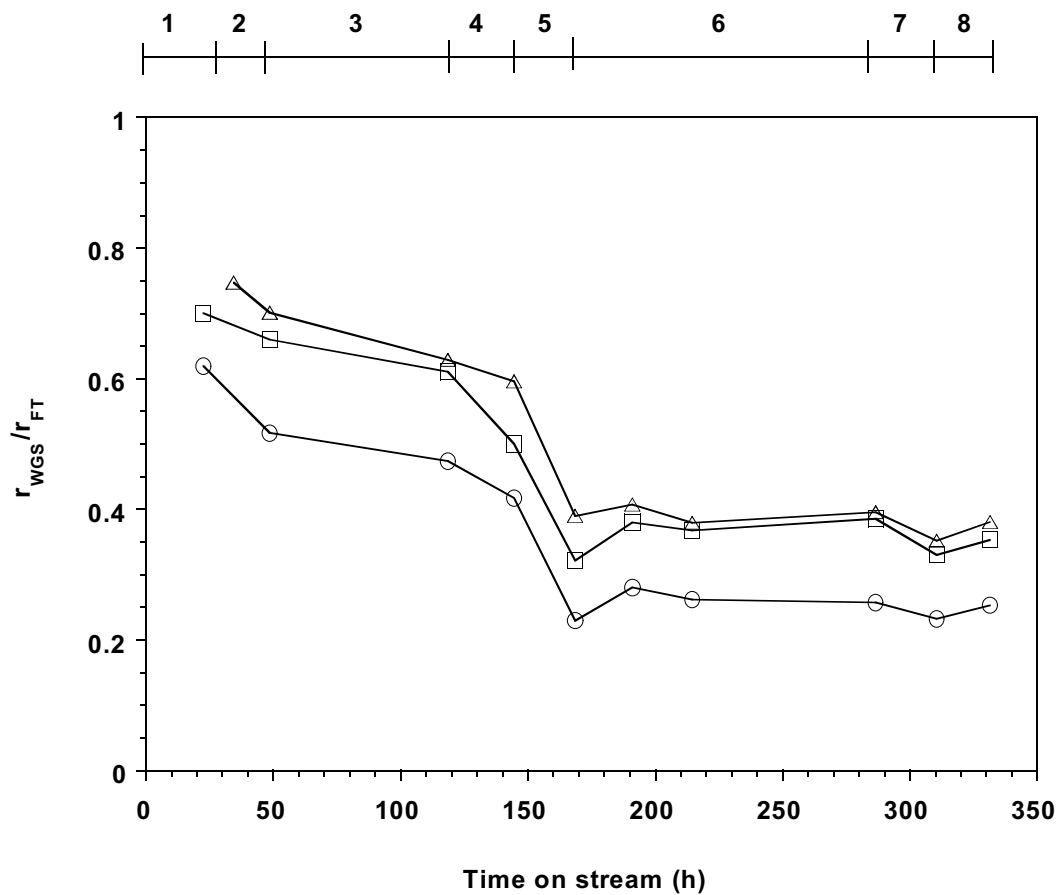


Figure 6. Ratio of water-gas shift rate to Fischer-Tropsch rate as a function of time on stream for (○), 100Fe/4.6Si/2.0Cu/1.44K, (□), 100Fe/4.6Si/2.0Cu/3.0K and (△), 100Fe/4.6Si/2.0Cu/5.0K catalysts. Conditions are identified on time line above graph.