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IMPROVED FISCHER-TROPSCH SYNTHESIS CATALYSTS FOR INDIRECT COAL LIQUEFACTION: FINAL QUARTERLY TECHNICAL PROGRESS REPORT NO. 4 FOR THE PERIOD 1 JULY TO 30 SEPTEMBER 1986

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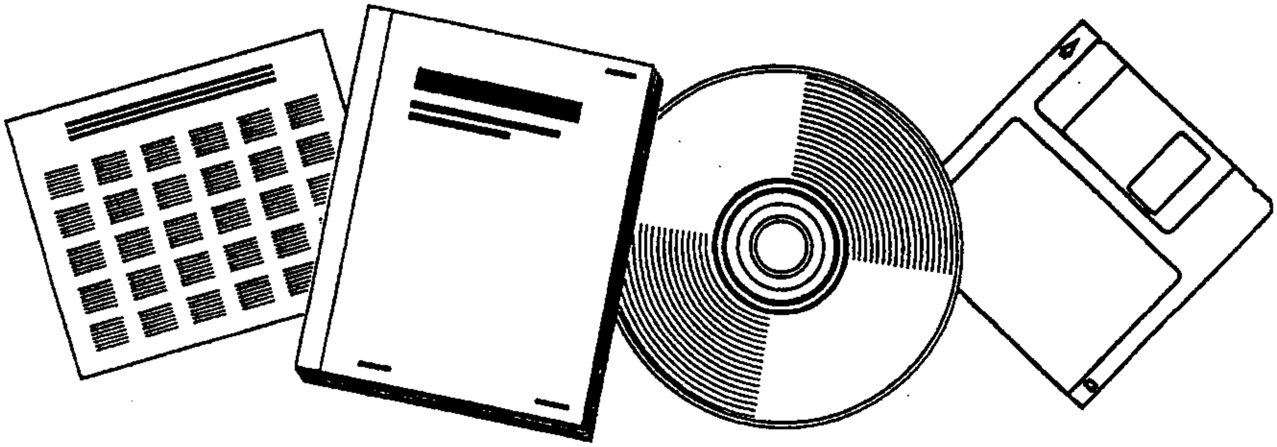

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IMPROVED FISCHER-TROPSCH SYNTHESIS CATALYSTS FOR INDIRECT COAL LIQUEFACTION

By: J. G. McCarty, R. B. Wilson, and G. T. Tong

Prepared for:

UNITED STATES DEPARTMENT OF ENERGY
Pittsburgh Energy Technology Center
P.O. Box 10940
Pittsburgh, Pennsylvania 15236-0940
Attention: Mr. Edgar B. Klunder, Project Manager

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Approved:

D. L. Hildenbrand
D. L. Hildenbrand, Director
Materials Research Laboratory

MASTER

SRI International

333 Ravenswood Ave. • Menlo Park, CA 94025
(415) 326-6200 • TWX: 910-373-2046 • Telex: 334-486

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SUMMARY

We have made significant progress in developing novel catalysts for the Fischer-Tropsch synthesis (FTS). The stoichiometries of the cluster synthesis and surface-confining reactions on an alumina support for aluminum tetra- and aluminum hexa-ruthenium hydridocarbonyl cluster catalysts were determined by gas evolution measurements. Characterization with FTIR and NMR spectroscopy of the cluster intermediates is also consistent with the observed cluster catalyst stoichiometry, Al_2O_3-$Al(C_2H_5)$-$Ru_4H_3(CO)_{12}$ and Al_2O_3-$Al(C_2H_5)$-$Ru_6H(CO)_{18}$. Activation of the surface-confined supported cluster complex by heating to 573 K in inert gas or hydrogen is likely to produce a stabilized cluster catalyst due to affinity of aluminum for alumina and the strength of the aluminum-ruthenium bonds relative to ruthenium-ligand bonds.

The cluster catalysts were tested for FTS in 2:1 H_2:CO syngas at 523 K and 1 atm. The 0.6 wt% Ru_4 catalyst had superior activity and about the same selectivity through C_8 hydrocarbons as a commercial alumina-supported 0.5 wt% Ru catalyst. The 1.2 wt% Ru_6 catalyst was less active but had similar selectivity. Further activation, characterization, and testing are necessary to determine if these cluster catalysts suppress wax formation and remain stable with respect to the formation of volatile carbonyls.

Substantial changes in selectivity of standard-fused iron catalysts were found following treatment to uniformly chemisorb submonolayer quantities of sulfur. Approximately 40% of a monolayer of sulfur was slowly adsorbed at 473 K on the potassium-promoted fused iron catalyst following reduction and passivation by accumulation of a surface layer of carbon and CO. The passivating layer was removed and the sulfur was locally dispersed by heating to 1000 K in hydrogen. The treated catalyst had a three-fold reduction in methane selectivity relative to untreated reduced fused iron at 573 K, and the C_2 olefin yield approached 100%

($C_2H_4/C_2H_6>20$). The C_{2+} production rate at 573 K was only about half that of the untreated catalyst per unit area and comparable to the activity of fused iron at 523 K per unit weight. Development of low-level sulfur-treated precipitated iron FTS catalysts with a higher surface area is in progress.

EXPERIMENTAL RESULTS

Task 1: Synthesis of Dual-Function Mixed-Metal Cluster Catalysts

Surface-confined Fischer-Tropsch synthesis (FTS) catalysts are to be synthesized in Task 1, using a pendant hydrocarbyl functional group that reacts with hydroxyl groups on the surface of an appropriate support material. This work is divided into the following subtasks:

A. Synthesis of hydridocarbonyl ruthenium clusters.

B. Reaction of hydridocarbonyl clusters with alkyl aluminum to give alkyl aluminum carbonyl ruthenium clusters.

C. Reaction of alkyl aluminum carbonyl ruthenium clusters with the support.

D. Synthesis of alkyl complexes of Fe, Ru, and Co.

E. Reaction of alkyl complexes with the support.

F. Reaction of alkyl complexes with hydridocarbonyl ruthenium clusters to give alkylcarbonyl clusters.

G. Reaction of alkylcarbonyl clusters with the support.

H. Synthesis of mixed-metal (Fe, Ru) hydridocarbonyl clusters.

I. Reaction of mixed-metal hydridocarbonyl clusters with alkyl aluminum to give alkyl aluminum mixed-metal carbonyl clusters.

J. Reaction of alkyl aluminum mixed-metal carbonyl clusters with the support.

K. Reaction of mixed-metal hydridocarbonyl clusters with alkyl complexes to give alkyl mixed-metal carbonyl clusters.

L. Reaction of alkyl mixed-metal carbonyl clusters with the support.

During the third quarter of 1986, progress was made in subtasks A through E of Task 1. A description of these subtasks and the progress to date follows.

Task 1A: Synthesis of Hydridocarbonyl Ruthenium Clusters. Two additional batches of hydridocarbonyl ruthenium clusters, $H_4Ru_4(CO)_{12}$ and $H_2Ru_6(CO)_{18}$, were synthesized and fully characterized. The infrared and NMR spectra and FTS testing results for these clusters and cluster catalysts were described in the previous quarterly report. However, the amount of material previously synthesized was not sufficient to allow elemental analysis, gas evolution, and extended FTS testing.

Tetrahydridoruthenium carbonyl is prepared by our method, the direct reaction of triruthenium dodecacarbonyl with hydrogen in hexamethyldisilazane (HMDS) at elevated temperature.

$$4/3\ Ru_3(CO)_{12} + 2\ H_2 \xrightarrow[135^0C]{HMDS} H_4Ru_4(CO)_{12} + 4\ CO \qquad (1)$$

The hexaruthenium cluster is synthesized by Shore's method.[1] Triruthenium dodecacarbonyl is reduced by sodium benzophenone ketal and then acidified.

$$Ru_3(CO)_{12} + Na[Ph_2(CO)] \xrightarrow[25^0C]{THF} 1/2\ Na_2[Ru_6(CO)_{18}] \qquad (2)$$

$$Na_2[Ru_6(CO)_{18} + 2\ HCl \xrightarrow[25^0C]{THF} H_2Ru_6(CO)_{18} + 2\ NaCl \qquad (3)$$

The FTIR and NMR results (Table 1) are in agreement with the literature[2-4] and indicate that the cluster solutions were pure. The infrared spectrum of $H_4Ru_4(CO)_{12}$ in cyclohexane solution exhibited the expected CO stretching bands at 2081(s), 2067(s), 2030(m), and 2024(s) cm^{-1}. The proton NMR spectrum of $H_4Ru_4(CO)_{12}$ in chloroform showed a singlet at -17.9 ppm. As reported in the previous quarterly, the infrared spectrum of $H_2Ru_6(CO)_{18}$ in dichloromethane solution exhibited (νco) bands at 2058(s) cm^{-1}, 2052(s) cm^{-1}, and 2003(w) cm^{-1}; the proton NMR spectrum of $H_2Ru_6(CO)_{18}$ in chloroform shows a singlet at 8.8 ppm.

Task 1B: Reaction of Hydridocarbonyl Ruthenium Clusters with Alkyl Aluminum. A novel aspect of our approach to synthesizing strongly bound ruthenium cluster catalysts is the intermediate synthesis of alkyl

Table 1

FTIR AND NMR SPECTRA OF RUTHENIUM HYDRIDOCARBONYL CLUSTERS

Cluster	FTIR bands (cm^{-1})[a]	NMR peaks (ppm)[b]
$H_4Ru_4(CO)_{12}$	2081(s), 2067(s), 2024(s), 2030(m)	−17.9 (sgl)
$H_2Ru_6(CO)_{18}$	2058(s), 2052(s) 2003(w)	+8.8 (sgl)
$C_2H_5)_2AlRu_4(H)_3(CO)_{12}$	2016(s), 1998(s), 2037(m), 2030(m), 1976(m)	5.22 (sgl) 4.10 (dbl) 2.01 (tpl)
$(C_2H_5)_2AlRu_6(H)(CO)_{18}$	NA	5.78 (sgl)

[a] (s), (m), (w) qualitatively refer to strong, moderate, and weak intensity in the solvent.

[b] (sgl), (dbl), (tpl), refer to singlet, AB doublet, and triplet peaks, respectively, in C_6D_6 solvent.

aluminum ruthenium carbonyl clusters just before reaction with support materials. Both of the tetraruthenium and the hexaruthenium hydridocarbonyl complexes react readily with triethyl aluminum at room temperature. The reaction stoichiometries were determined by measuring the quantity of ethane produced. Gas chromatography indicated that only ethane was released; no trace of carbon monoxide was detected. Various amounts of ruthenium clusters (from 0.15 to 1.5 mmol) were used to react with excess triethyl aluminum to determine the reaction stoichiometries. For both the tetraruthenium cluster and the hexaruthenium cluster, the results are consist with the production of one equivalent of ethane.

$$H_4Ru_4(CO)_{12} + Et_3Al \xrightarrow[25\ C]{THF} (Et_2Al)Ru_4(H)_3(CO)_{12} + EtH \qquad (4)$$

$$H_2Ru_6(CO)_{18} + Et_3Al \xrightarrow[25\ C]{THF} (Et_2Al)Ru_6(H)(CO)_{18} + EtH \qquad (5)$$

The reactions were allowed to continue overnight to assure complete reaction. In both cases, the color changed from yellow ($H_4Ru_4(CO)_{12}$) or purple ($H_2Ru_6(CO)_{18}$) to dark brown. Spectroscopic changes were also observed in the ^{1}HNMR and infrared spectra. The reaction of $H_4Ru_4(CO)_{12}$ and Et_3Al in benzene-D_6 was followed by ^{1}HNMR. New peaks appeared at 5.22 (singlet) ppm, 4.10 (AB doublet) ppm, and 2.01 (triplet) ppm and are tentatively assigned to the hydride, methylene protons, and methyl protons, respectively, of the $(Et_2Al)\ Ru_4(H)_3(CO)_{12}$ complex. The infrared spectrum of this new species in THF solution exhibited CO vibrational bands at 2037(m), 2030(m), 2016(s), 1998(s), and 1976(m) cm^{-1}. To determine the exact structure of $(Et_2Al)Ru_4(H)_3(CO)_{12}$ and $(Et_2Al)Ru_6(H)(CO)_{13}$, we are attempting to isolate these two new compounds.

Task 1C: Reaction of Alkyl Aluminum Carbonyl Ruthenium Clusters with the Support. The two alkyl aluminum carbonyl ruthenium clusters, $(Et_2Al)Ru_4(H)_3(CO)_{12}$ and $(Et_2Al)Ru_6(H)(CO)_{18}$, each readily reacts with the -alumina. The Bronsted acid site density of alumina (1 mmol/g) was determined by titration with ethyl lithium as described in the previous quarterly report. Excess hydroxyl groups are available for reaction with the clusters if the metal loading is less than a few weight percent. The stoichiometries of the surface-confining reaction of the clusters with the supports were again determined by measuring the amount of ethane produced. The reactions were also monitored by gas chromatography of the evolved gas. Again, no carbon monoxide was released. Only one equivalent of ethane is produced with respect to the ruthenium cluster used.

$$(Et_2Al)Ru_4(H)_3(CO)_{12} + (AlO){-}OH \text{ support} \xrightarrow[25^{\circ}C]{THF}$$

$$(AlO){-}O{-}Al(Et)Ru_4(H)_3(CO)_{12} + EtH \qquad (6)$$

$$(Et_2Al)Ru_6(H)(CO)_{18} + (AlO){-}OH \xrightarrow[25^{\circ}C]{THF}$$

$$(AlO){-}O{-}Al(Et)Ru(H)(CO)_{18} + EtH \qquad (7)$$

Elemental analyses of the tetraruthenium cluster and hexaruthenium cluster catalysts on β-alumina were performed by a commercial analytical laboratory. The results (Table 2) indicate ruthenium loadings of 0.61 wt% and 1.26 wt% for the Ru_4 and Ru_6 cluster catalysts, respectively.

Task 1D: Synthesis of Alkyl Complexes of Fe, Ru, and Co. During this quarter, we completed the synthesis of the alkyl complex of ruthenium $[(allyl)_2\ Ru(CO)_2]$. The procedure for synthesizing this compound is shown in the following equations:

$$Ru_3(CO)_{12} + 3\ (allyl)Br \longrightarrow 3\ (allyl)Ru(CO)_3Br + 3\ CO \qquad (8)$$

$$(allyl)Ru(CO)_3Br + 2\ Na\ Hg \rightarrow Na^+[(allyl)Ru(CO)_3]^- + NaBr \qquad (9)$$

$$Na^+[(allyl)Ru(CO)_3]^- + (allyl)Br \rightarrow (allyl)_2Ru(CO)_2 + CO + NaBr \qquad (10)$$

Table 2

ELEMENTAL AANALYSIS OF RUTHENIUM CLUSTER CATALYSTS SUPPORTED ON -ALUMINA

Cluster	Ru	C	H
Ru_4	0.61	5.09	1.04
Ru_6	1.26	9.77	1.84

[a] Balance: Al, O, or Al_2O_3.

The last step (10) was performed in THF solution at room temperature overnight. The first two steps (8, 9) were described in the previous quarterly report. The one equivalent of carbon monoxide released was detected by gas chromotography of the evolved gas. The resulting yellow solution of $(allyl)_2Ru(CO)_2$ was used to react with supporting material as described in subtask 1E.

Task 1E: Reaction of Alkyl Complexes with the Support. The tetrahydrofuran solution of $(allyl)_2Ru(CO)_2$ prepared from subtask 1D was used to react with β-alumina following well-known methods[5]. However, no gas product (e.g., propylene, propane, carbon monoxide) could be detected by gas chromatography. Therefore, the metal complex may simply absorb on the support or the alkyl may have been released in the form of alcohol. Further investigation of this reaction is under way.

Task 2: Sulfur Treatment of the Fischer-Tropsch Catalysts

In the previous quarter, we demonstrated that high-level sulfur-treated standard fused iron catalyst (UCI C73-1-01) significantly suppressed methane formation. Pretreatment of a fresh catalyst below half saturation coverage was performed to restore FTS activity while continuing to suppress methane production. A low uniform level of sulfur coverage was achieved by slowing the rate dissociative chemisorption of H_2S on the catalyst surfaces so that surface reaction rather than pore diffusion limited the net rate of sulfur uptake.

The reduced metal surface was passivated by CO adsorption, dissociation, and disproportionation to CO_2 at 473 K. Aliquots of 100 kPa CO were injected into a closed gas recirculation loop containing 1 g of the reduced fused iron catalyst while the $CO-CO_2$ ratio was followed with an on-line mass spectrometer. Approximately 200 μmol of carbon monoxide was injected, corresponding to two monolayers of adsorbed CO. Some CO_2 evolution was observed, and most of the CO was consumed during passivation.

Following passivation, aliquots of 0.96% H_2S/H_2 were injected into the closed recirculation loop at 473 K while the gas-phase H_2S concentration was monitored with a sensitive photoionization detector as described in the previous quarterly report. Approximately, 200 μmol of hydrogen sulfide was injected into the system representing approximately 0.2 monolayer sulfur capacity of the catalyst. The gas-phase H_2S concentration slowly fell to 15 ppm after 2 hours. The system was then flushed with pure hydrogen at 343 K. The deposited carbon, iron carbide, and adsorbed CO were removed by temperature-programmed reaction (TPR) to 873 K in 100 kPa flowing hydrogen. Methane, but no hydrogen sulfide, was observed during the TPR, indicating that the chemisorbed sulfur was irreversibly bound during removal of the passivating layer.

The catalyst was held at 825 K in recirculating hydrogen for 12 hours to allow local microscopic surface diffusion and equilibration. Gas-phase hydrogen sulfide concentrations were measured over a range of temperatures and the final sulfur chemisorption isostere was determined (Figure 1). The catalyst was further passivated by CO adsorption at room temperature before removal from the recirculation system and transfer to the FTS testing system. The catalyst was reduced in flowing hydrogen at 523 K before FTS testing as described in Task 3 below.

The actual fractional sulfur coverage could not be accurately determined. Based on the previous high-level sulfur treatment (near full monolayer sulfur coverage), the sulfur coverage would have been 0.2 monolayer. However, during measurement of the isostere the temperature approached 1000 K, which may have caused sintering. The BET surface areas of the freshly reduced fused iron catalyst (30 m/g) and the low-level treated catalyst (7 m/g) showed a factor of 4 reduction in total surface area. The effect of K_2O on total surface area is not known; thus the BET measurements suggest $0.2 < \theta_s < 0.8$ monolayer. Compared with isosteres for monolayer powdered iron[6], the low-level sulfur treated fused iron would have approximately 0.4 monolayer sulfur coverage (see Figure 1).

Task 3: Characterization and Testing of FTS Catalysts

Catalyst Preparation. The tetraruthenium cluster and hexaruthenium cluster catalysts synthesized in Task 1 were activated *in situ* in the

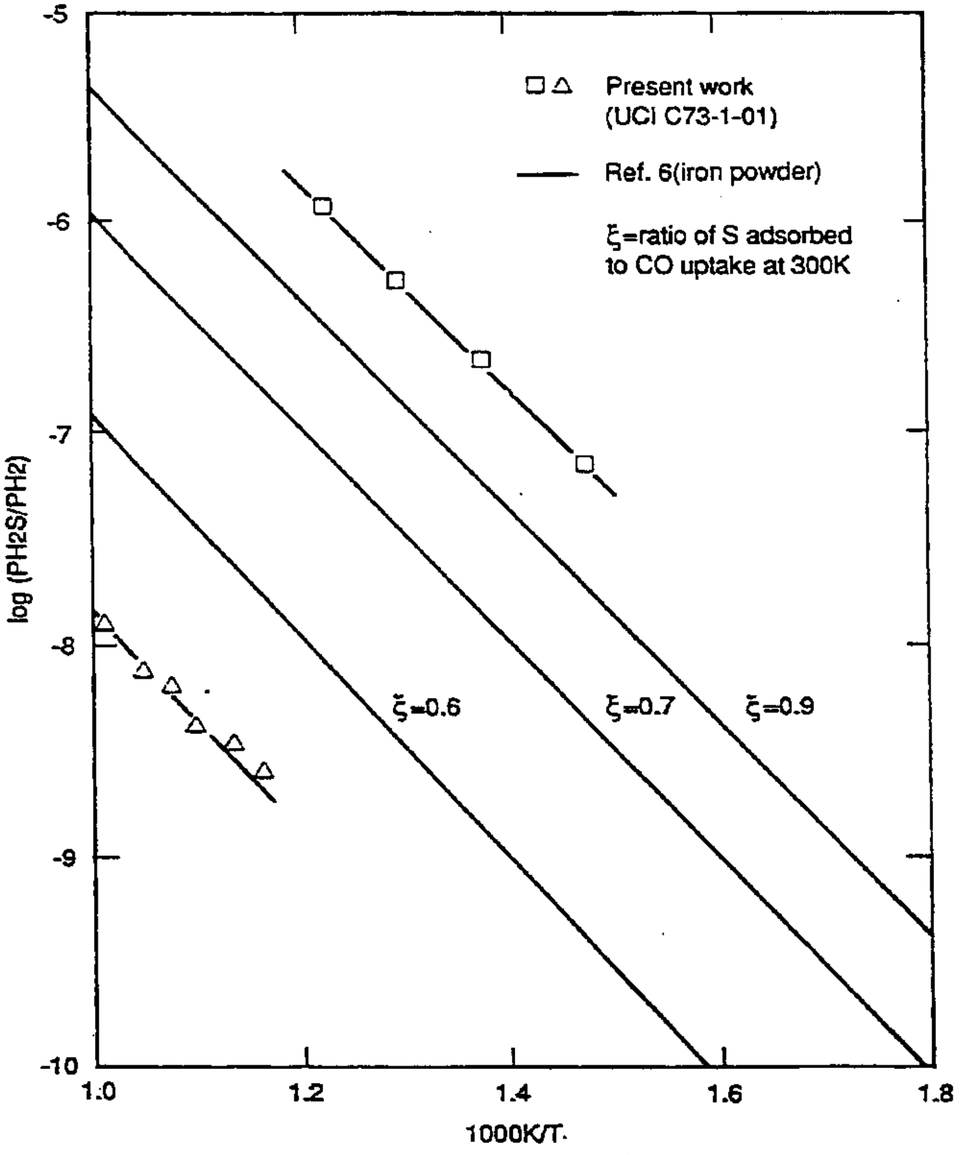

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FIGURE 1 SULFUR CHEMISORPTION ISOSTERES ON FUSED IRON AND IRON POWDER characterization and FTS testing apparatus by temperature-programmed reaction (TPR) from 300 K to 573 K in 100 kPa hydrogen at a heating scale of 0.167 K/s. Methane was detected during the activation, and the reaction appeared to go to completion, indicating removal of all carbonyl ligands. This result is in contrast with activation in helium where only partial CO removal was observed. Additional TPD, TPR studies of the activation of the Ru_4 and Ru_6 clusters are planned for the next quarterly reporting periods.

The conventional ruthenium on alumina catalyst was obtained from Engelhard in the form of 1/8-inch pellets with 0.5 wt% metal loading. This catalyst was used as received without any reduction because it is skin-coated (egg-shell type) and grinding may cause nonuniformity in catalyst sample preparation.

The final sulfur coverage on the fused iron catalyst prepared under Task 2 was about half saturation. The previously prepared high-level sulfur treated catalyst (0.8 monolayer sulfur) was also tested. Typically, 0.5 g of the catalysts was used. The Fischer-Tropsch synthesis reaction was conducted with 100 kPa synthesis gas of fixed composition (H_2:CO = 2:1) at 573 K under differential reaction conditions.

FTS Testing Results. All the Fischer-Tropsch synthesis experiments were conducted under differential conditions with a maximum CO conversion of 10%. The hydrocarbon reaction rate R is defined as the number of micromoles of carbon monoxide converted into C_1 through C_{10} hydrocarbon per gram of catalyst per second (Table 3). The selectivity S is defined as the ratio of the rate of formation of methane relative to the overall hydrocarbon reaction rate for C_1 through C_{10} products (on a carbon atom basis).

Both the tetraruthenium cluster and hexaruthenium cluster catalysts synthesized in Task 1 were more active than the conventional alumina-supported ruthenium catalyst at 523 K. Both cluster catalysts had a methane selectivity of 63% and chain growth probability of 0.51. However, the tetramer Ru catalyst was 50% more active than the hexamer Ru catalyst. If metal weight loadings were considered for these catalysts,

Table 3

HYDROCARBON PRODUCT RATES[a] (nmol/g cat/s)

Catalyst	Temp (K)	Total	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	α[b]	β[c]	Methane[d] Selectivity
Clean fused iron	573	92 (34)[e]	57.8	24.1	5.37	2.46	1.19	0.52	0.26	-	-	-	0.465	-	42
Sulfided fused iron $\theta_s = 0.5$	573	5.1 (3.6)[e]	1.52	1.91	0.96	0.46	0.20	0.058	-	-	-	-	0.421	21.9	14
Sulfided fused iron $\theta_s = 1.0$	573	0.67 (0.43)[e]	0.24	0.22	0.13	0.055	0.017	0.006	-	-	-	-	0.383	-	18
0.5% Ru on Al_2O_3	573	131 (12)[e]	119.3	7.80	2.77	0.73	0.41	0.23	0.14	-	-	-	-	0.026	82
Tetraruthenium cluster (~ 0.6 wt% Ru)	523	27 (3.2)[e]	22.4	2.26	1.46	0.48	0.28	0.15	0.074	0.045	0.035	0.02	0.506	0.005	63
Hexaruthenium cluster (~ 1.2 wt% Ru)	523	19 (3.2)[e]	15.7	1.58	0.86	0.39	0.18	0.10	0.056	0.034	0.027	0.02	0.515	0.0	63

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[a] Paraffins and olefins.

[b] Chain growth probability factor.

[c] Ratio of C_2 olefin to C_2 paraffin.

[d] C_1 rate/(total rate) x 100%.

[e] Total hydrocarbon product rate excluding C_1.

then the tetramer Ru catalyst was twice as active as the hexamer Ru catalyst. The conventional 0.5 wt% ruthenium on alumina catalyst was slightly more active than the clean fused iron catalyst at 573 K; however, its selectivity toward methane was high, about 82%.

The sulfided catalysts demonstrated preferential suppression of methane formation and preferential olefin production. The selectivity toward methane was 14% for the low-level sulfided catalyst and 18% for the high-level sulfided catalyst as compared with 42% for the untreated catalyst. The ratio of ethylene to ethane was about 20 for both sulfided catalysts. The higher paraffins and olefins have not yet been determined because of the lack of analytical standards; however, it is reasonable to assume that C_3 to C_5 hydrocarbons produced from these sulfided catalysts were also highly olefinic. The chain growth probability for C_2 to C_7 hydrocarbons was reduced slightly as the amount of sulfur chemisorbed on the catalyst's surface increased.

Unlike the reduced untreated fused iron catalyst, both the low-level and high-level sulfided fused iron catalysts showed increased evolution of CO_2 and hydrocarbon products with syngas exposure time. After 24 hours, the total hydrocarbon rate at 573 K for the low-level sulfided catalyst was 5.5% of the rate of the untreated catalyst and 0.7% for the high-level sulfided catalyst. If only C_2 to C_7 total hydrocarbon rates were considered, the activity of the low-level sulfided catalyst was 11% of the clean catalyst, and the activity of the high-level sulfided catalyst was 1.3%.

DISCUSSION

Ruthenium Cluster Catalysts

The novel aspect of our synthesis of a stable ruthenium cluster is the intermediate synthesis of aluminum ruthenium cluster before the surface-confining reaction with acidic sites on the support. The strong intermetallic aluminum-ruthenium bond is likely to remain unbroken during the surface-confining reaction and activation in a reducing atmosphere. Clusters catalysts prepared by adsorption and decomposition of carbonyls or through reaction of an alkyl ligand with an acid site create an oxygen-ruthenium bond. Such preparations may suffer from desorption and agglomerization in reducing atmospheres of H_2 or CO due to the weaker, more reducible metal-support bond, as is known for most supported carbonyl or allyl complexes. Our studies of the Al-Ru complex formation reaction and the surface-confining reaction show minimal loss of ligands. Preliminary studies of the activation process indicate that the complexes are stable, but additional activation and characterization experiments are needed to verify the stability of the supported clusters.

Evidence thus far indicates that the ruthenium cluster catalysts have greater activity than, but selectivity similar to, conventional alumina-supported ruthenium catalysts. If we assume that the clusters are 100% dispersed, as we expect, and the conventional ruthenium catalyst is 50% dispersed, then the tetramer cluster catalyst has twice the C_{2+} production rate per surface ruthenium atom relative to the conventional catalyst when extrapolated to 573 K. In contrast, the hexamer cluster has about half the activity of the conventional catalyst per surface site. A more definitive comparison of activity will be possible after we have completed additional activation and characterization experiments, especially H_2 and CO titration.

The hydrocarbon product distribution for the cluster catalysts does not appear to differ from that of conventionally supported ruthenium. The chain growth probability for both cluster catalysts is comparable to that reported for supported Ru[7] and our results for the Engelhard Ru catalyst. We had anticipated a cutoff in higher hydrocarbon yield due to the small size of the clusters. Such a cutoff was not evident through C_8 hydrocarbons. Additional testing (perhaps in a slurry reactor configuration) is necessary to determine if a sharp decrease in the chain growth exists in the waxy hydrocarbon range. We also expect to synthesize cluster catalysts with zeolite and molecular sieve supports to further suppress the formation of waxes.

The high activity of the 0.6 wt% Ru cluster catalyst is encouraging. At this point in the project, the alumina-supported ruthenium tetramer catalyst has FTS activity comparable to fused iron and should be viewed as a potential low temperature slurry reactor catalyst. The principal concerns are (1) stability at lower temperature and higher pressure due to formation of carbonyls, (2) the methane selectivity, which appears greater than for fused iron, and (3) suppression of waxes. However, before additional tests are performed with this catalyst, we have several additional catalyst formulations and activation/FTS testing experiments to perform.

Sulfur-Treated Iron FTS Catalysts

The selectivity of the low-level sulfur fused iron catalyst with almost a three-fold reduction in methane yield and nearly 100% olefin selectivity for the light hydrocarbons is most encouraging. The roughly five-fold decrease in activity can be offset by the higher operating temperature; i.e., the sulfur-treated catalyst operating at 573 K has about the activity for C_{2+} hydrocarbon production as the untreated catalyst at 523 K. The adequate activity, the low methane selectivity, and the high selectivity for light olefins make this catalyst a good candidate for FTS in a fluid bed or fixed bed reactor operating above 550 K to suppress wax production by lowering the Shultz-Flory-Anderson chain growth parameter.

Sulfur-treated iron FTS catalysts may have other beneficial properties in addition to improved product selectivity. One possibility (to be determined) is that the activity is more strongly dependent on pressure than for the untreated catalysts. This increased pressure-dependence follows because of the decreased binding strength for both chemisorbed hydrogen and carbon monoxide due to the presence of uniformly distributed surface sulfur. The reaction order for production of hydrocarbons (the dependence of the log FTS rate on log partial pressure) is typically less than 1 for H_2 and 0 or < 1 for CO, indicating that the active surfaces are near full occupation with adsorbed intermediates. Weakened CO and H adsorption could free reaction sites, thereby increasing the synthesis rate.

Another possible desirable property could be increased coking resistance. Steam reforming catalysts are known to have increased resistance to coke formation by the fractional adsorption of (low-level) sulfur. Work in our own laboratory has confirmed this for Ni and Ru catalysts. Deposition of catalyst carbon is associated with surface planes of high coordination (those containing steps or ledges), which may be responsible for methane formation and are known to preferentially bind adsorbed sulfur atoms on nickel surfaces. Increased coking resistance could allow FTS reaction with a higher CO-to-hydrogen ratio, perhaps to 1:1, or greater, thereby increasing olefin and higher hydrocarbon yields while using less expensive synthesis gas processes following the gasifier. Task 4, scheduled for the summer of 1987, is intended to provide data to verify these possibilities.

TECHNICAL STATUS

The following work has been performed during the past quarter:

- Completed FTS testing for clean, low-level, and high-level sulfur-treated fused iron catalysts.
- Completed characterization and FTS testing of Ru_4 and Ru_6 hydrocarbonyl clusters and alumina-supported cluster catalysts.
- Synthesized $(Allyl)_2Ru(CO)$ organometallic monomer intermediate and prepared an alumina-supported Ru catalyst.

During the next quarterly period (October-December 1986), we expect to perform the following tasks:

- Synthesize, characterize, and test for FTS activity and selectivity a series of Ru, Ru_4, Ru_6 cluster catalysts supported on zeolites.
- Activate the Ru, Ru_4, Ru_6 catalysts on alumina and zeolite supports in inert gas and hydrogen and compare the resulting FTIR spectra and FTS test results.
- Prepare, characterize, and test for FTS fresh and low-level sulfur-treated precipitated iron catalysts.

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