

NOVEL SLURRY PHASE DIESEL CATALYSTS FOR COAL-DERIVED SYNGAS

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## Abstract

This report describes research conducted to support the DOE program in novel slurry phase catalysts for converting coal-derived synthesis gas to diesel fuels. The primary objective of this research program is to develop attrition resistant catalysts that exhibit high activities for conversion of coal-derived syngas. Three partner institutions, University of New Mexico (UNM), Texas A&M University (TAMU) and Brigham Young University (BYU) have actively worked together to develop these novel catalysts.

Specifically, at TAMU we have synthesized several alumina (from Condea) and silica (Davison 948) supported iron Fischer-Tropsch (F-T) catalysts, determined their attrition properties (in collaboration with the UNM) under both reactive and non-reactive conditions, and evaluated their performance during F-T synthesis in a stirred tank slurry reactor (STSR). Also, we have determined attrition properties of a precipitated iron F-T catalyst with nominal composition 100 Fe/3 Cu/4 K/16 SiO<sub>2</sub> (in parts by weight) in a STSR under both reactive and non-reactive conditions. This catalyst was developed at TAMU under DOE sponsorship (Contracts DE-AC22-89PC89968 and DE-AC22-94PC93069) and has excellent performance characteristics: high activity and productivity, excellent stability with time and high selectivity to liquid hydrocarbons and wax.

During extended F-T synthesis tests in the STSR we found that the alumina supported catalysts showed formation of fine particles (about 15 wt%) in the size range of 1-10 μm. The silica supported catalyst was more resistant to erosion than the alumina supports. Attrition resistance behavior of the precipitated TAMU catalyst was comparable to or better than that of Davison 948 silica in both types of attrition tests (ultrasound fragmentation and STSR tests). Its attrition resistance could be further improved by preparing the catalyst in form of micro-spherical particles (e.g. by spray drying).

Alumina supported catalyst (20wt% Fe/γ-alumina; promoted with 1.6 wt% of Cu and K) had higher initial activity and better selectivity to C<sub>5</sub>+ hydrocarbons than the silica supported catalyst (20wt% Fe/silica; promoted with 1.6 wt% of Cu and K) but it deactivated more severely. Further work is needed to improve stability and selectivity of supported catalysts.

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## **Executive Summary**

This report covers a three year period of cooperative research grant under the University Coal Research program. This research program involves a partnership between three institutions, University of New Mexico (UNM), Texas A&M University (TAMU) and Brigham Young University (BYU). The three partner institutions have actively worked together to develop novel catalysts for converting coal-derived synthesis gas to diesel fuels. The catalysts were designed for slurry phase Fischer-Tropsch synthesis, which is recognized as the preferred mode for operation of F-T reactors. Slurry phase catalysts based on Fe tend to break down into fine particles leading to severe operational difficulties in separating the hydrocarbon products from the catalyst. The primary objective of this research program has been to develop attrition resistant catalysts that exhibit high activities for conversion of coal derived syngas ( $H_2/CO$  feed ratio of  $\sim 2/3$ ).

Studies conducted at TAMU were focused on synthesis of supported Fe catalysts, evaluation of their attrition properties in a stirred tank slurry reactor (STSR) under both reactive and non-reactive conditions, F-T synthesis reaction studies in STSR to determine activity, selectivity and stability of supported catalysts. Also, we have determined attrition properties of a precipitated iron F-T catalyst with nominal composition 100 Fe/3 Cu/4 K/16  $SiO_2$  (in parts by weight) in a STSR under both reactive and non-reactive conditions. This catalyst was developed at TAMU under DOE sponsorship (Contracts DE-AC22-89PC89968 and DE-AC22-94PC93069) and has excellent performance characteristics: high activity and productivity, excellent stability with time and high selectivity to liquid hydrocarbons and wax. However, its attrition properties have not been determined yet. Here we briefly summarize the major accomplishments and results.

### Catalyst Synthesis

Several catalysts were prepared by aqueous incipient wetness impregnation (IWI) of commercially available alumina (Condea HP 14 and Condea HP 14-150) and silica (Davison 948) supports. All synthesized catalysts had iron loading of 20 wt%. Copper (Cu) and potassium (K) were used as standard promoters, in the following proportions relative to iron: 100 Fe/8 Cu/8 K (in parts per weight), which corresponds to 1.6 wt% loading for each of the two promoters. With the Davison 948 silica support catalysts were prepared by both aqueous and organic (methanol as solvent) impregnation to study the effect of preparation procedure on catalytic performance.

### Attrition Properties of Supported and Precipitated Catalysts

Commercially available supports were tested first for their attrition resistance using the ultrasonic fragmentation test at the UNM. The more promising supports were tested then by TAMU in a STSR, where either  $N_2$  gas or syngas was bubbled during stirring to simulate the mechanical forces that would be encountered during slurry phase reactor operation. Subsequently, UNM performed particle size and SEM tests of these supports and/or catalysts to correlate the ultrasonic test results with those from the more extended testing in a STSR.

Alumina supports (Condea HP 14 and Condea HP 14-150) showed evidence of significant fracture, and some break-up due to erosion, during the ultrasonic fragmentation tests. Davison 948 silica and precipitated TAMU catalyst were resistant to ultrasonic fragmentation, and showed very little erosion. Several of these supports were then tested in a stirred tank reactor under simulating F-T synthesis reaction conditions for 168 hours. We found that the STSR testing may be more severe to erosion in terms of its effect on the break-up of the support particles. However, both the alumina and Davison 948 silica supports were found to be sufficiently strong for further testing under reaction conditions. In the next step, the synthesized F-T catalysts were tested under actual F-T reaction conditions for extended times (up to 318 hours). With the alumina supported catalysts fine particles in the size range of 1-10  $\mu\text{m}$  were generated (about 15 wt%). The silica supported catalyst (Davison 948) is more resistant to erosion than the alumina supported catalysts. Attrition resistance behavior of the precipitated TAMU catalyst was comparable to or better than that of Davison 948 silica in both types of tests (ultrasound fragmentation and STSR tests). Its attrition resistance could be further improved by preparing the catalyst in form of micro-spherical particles (e.g. by spray drying).

### Catalyst Testing in a STSR

Results from tests with Cu and K promoted Fe catalysts prepared by aqueous IWI of supports, showed that calcined  $\gamma$ -alumina (HP 14-150) is a more promising support than boehmite alumina (HP 14) for F-T synthesis. Calcination of  $\gamma$ -alumina is an important step, and the catalyst prepared by IWI of calcined support (at 500°C for 5 hours) was superior to the one prepared by IWI of uncalcined (as received) support. Silica supported catalyst had both lower initial activity and selectivity to  $\text{C}_5+$  hydrocarbons than the calcined  $\gamma$ -alumina supported catalyst, but it deactivated less severely. Improvements in stability are needed for both silica and alumina supported catalysts.

With Cu and K promoted 20% Fe/SiO<sub>2</sub> catalysts, the catalyst prepared from methanol solution had better activity maintenance than the catalyst prepared from aqueous solution. However, the initial catalyst activity was the same for both catalysts. Hydrocarbon selectivity of the catalyst prepared by organic IWI was inferior (more methane and less  $\text{C}_5+$  products) compared to the catalyst prepared by aqueous IWI. The expected promotional effects of K (increase in molecular weight of hydrocarbon products, increased olefinicity, increase in WGS activity) were observed to a relatively small extent on the catalyst prepared by aqueous impregnation, but were less evident on the catalyst prepared by organic impregnation. F-T activity was not significantly affected by addition of Cu and K promoters. The amount of K promoter used is rather high (8 parts per 100 parts of Fe on weight basis) compared to Fe precipitated catalysts, but its promotional effect was small. This is indicative of promoter-support interactions and/or decreased Fe-K contact.

Silica and alumina supported catalysts produced significantly more methane (4-8 % on carbon atom basis) than the precipitated TAMU catalyst (~2.5 %). Also, both their activity and stability were inferior in comparison to that of the precipitated catalyst. Further work is needed to develop basic understanding of underlying causes for differences in the reaction behaviors and to synthesize improved supported Fe catalysts for slurry phase F-T synthesis.

## Technical Objectives

The objective of this research project is to develop attrition resistant catalysts that exhibit high activities for conversion of coal-derived syngas to produce diesel fuels. The overall program is divided into the following tasks:

- Task 1. Project Orientation and Equipment Testing
- Task 2. Catalyst Synthesis and Characterization
- Task 3. Attrition Resistance Tests
- Task 4. Catalyst Testing and Data Analysis

In task 1, TAMU will prepare their fixed-bed and slurry reactors, and get their analytical system including gas chromatographs ready for product analysis. Shakedown runs with reactors will be conducted, and standard mixtures representative of F-T products (aqueous phase, organic phase and wax) will be analyzed.

In task 2, synthesis and characterization of precipitated and supported Fe catalysts will be performed collaboratively at BYU, TAMU and UNM. Characterization of these catalysts includes H<sub>2</sub> chemisorption, BET surface area measurements, SEM, TEM, XRD and Mössbauer studies to map out the microstructure of the prepared catalysts. Temperature programmed reduction (TPR) as well as isothermal reduction studies in a TGA will measure the reducibility of the catalysts synthesized.

In task 3, attrition tests at the micro-scale will be performed at UNM using the ultrasonic fragmentation approach. In addition, attrition tests will be performed in a stirred tank slurry reactor (STSR) at TAMU. Particle size distributions will be measured at UNM by a sedigraph particle size analyzer after extraction of the wax from the powder. Both TEM and SEM will be used at UNM to investigate the mechanism of attrition - erosion vs. fracture.

In task 4, selected catalysts will be evaluated in a STSR (TAMU) or a fixed bed reactor (BYU). Slurry samples from the STSR runs will be periodically withdrawn from the reactor in an inert atmosphere for particle size distribution measurements and catalyst characterization at UNM and/or BYU.

## **Description of Technical Progress**

### **Task 1. Project Orientation and Equipment Testing**

Shakedown tests in fixed bed and slurry reactors were successfully completed to test the equipment for reaction studies. Graduate students and postdoctoral fellows were trained in the use of gas chromatographs for product quantification, as well as the existing software for data analysis.

### **Task 2. Catalyst Synthesis and Characterization**

Catalysts synthesized at TAMU were prepared by incipient wetness impregnation (IWI) of commercially available alumina and silica supports. All synthesized catalysts had iron (Fe) loading of 20 wt%. Copper (Cu) and potassium (K) were used as standard promoters, in the following proportions relative to iron: 100 Fe/8 Cu/8 K (in parts per weight).

#### *Experimental*

##### 2.1a Preparation of Catalysts by Aqueous Incipient Wetness Impregnation

Commercial supports were first dried for 2 hours at 110°C in a vacuum, then sieved to 325-140 mesh (45-106 µm). The sieved support was calcined for 5 hours at 500°C (heating rate of 5°C/min) without gas flow, and then cooled down to a room temperature.

Catalysts were prepared by co-impregnation with aqueous solutions containing desired amounts of iron nitrate, copper nitrate and potassium bicarbonate in one (silica supported catalysts) or two (alumina supported catalysts) steps using the incipient wetness method. Impregnation was conducted by placing the desired amounts of support and aqueous solution of iron and promoter salts in small Teflon coated container (6.5 cm in diameter, 8 cm in height) and its content was stirred with a Teflon bar.

After each impregnation, the resulting mixture was transferred into a rotating shaft evaporator and the water was partially removed by creating a vacuum for 2.5 hours in a water bath at 50°C. The catalyst precursor was then transferred into a glass tube and dried in flowing air (100 ml/min) at 105-110°C for 5 h.

After the final impregnation/drying step the catalyst precursor was heated in flowing air (3 Nl/g-cat/h) from room temperature to 180°C at 1°C/min, held for 2 hours at 180°C to decompose any remaining nitrates. After this the air temperature was increased to 300°C (at 1°C/min) and held at 300°C for another 5 h. After cooling in air, the catalyst was crushed (alumina supported catalysts only) and sieved to 325-140 mesh (45-106 µm).

##### 2.1b Preparation of Catalysts by Organic Incipient Wetness Impregnation

Preparation of unpromoted 20% Fe, and 100 Fe/8 Cu/8 Na on Davison 948 silica catalysts by organic IWI was identical to that described for aqueous IWI, except that methanol was used as a solvent, instead of water. The impregnation was completed in four steps due to lower solubility of Fe, Cu and Na nitrate salts in methanol relative to water. Preparation procedure



for catalysts containing 20 wt% Fe and Cu and K as promoters was slightly different, due to low solubility of potassium salts in methanol. This catalyst was first impregnated with Fe and Cu salts, and then with potassium acetate dissolved in methanol. Davison 948 silica was first co-impregnated with nitrate salts of Fe and Cu dissolved in methanol. This was accomplished in four steps with drying between each step as described above for catalysts prepared by aqueous impregnation. After the final impregnation the catalyst was calcined in flowing air (see above). Following this the catalyst was impregnated with the desired amount of potassium acetate salt dissolved in methanol in one step. The impregnated catalyst was placed in the evaporator, followed by drying in air, and finally heated and calcined at 300°C for 5 hours.

### 2.1c Synthesis of Precipitated Iron Catalyst (100 Fe/3 Cu/4 K/16 SiO<sub>2</sub>, 59.7 wt% Fe)

Catalyst preparation consisted of three distinct steps: preparation of the iron-copper precursor, incorporation of silica binder, and impregnation by potassium. The constant - pH precipitation technique used to prepare the Fe/Cu catalyst precursor was described in detail previously (Bukur et al., 1989, 1990a). In brief, the catalyst precursor was continuously precipitated at 82°C from a flowing aqueous solution containing iron and copper nitrates at the desired Fe/Cu ratio, using aqueous ammonia. The precipitate was then thoroughly washed with distilled water by vacuum filtration. Silicon oxide was incorporated by addition of an appropriate amount of dilute (26 wt%) K<sub>2</sub>SiO<sub>3</sub> solution to undried, reslurried Fe/Cu coprecipitate, followed by adjustment of pH to  $\leq 6$  to ensure complete deposition of the silicate.

After a vacuum drying step, the potassium promoter was added as aqueous KHCO<sub>3</sub> solution via an incipient wetness pore filling technique. The final step was to dry the catalyst at 120°C for 16 hours in a vacuum oven. The dried catalyst was calcined in air at 300°C for 5 h, and then crushed and sieved to 45-106  $\mu\text{m}$  size range (140/325 mesh sieves).

### 2.2 Isothermal Reduction by Thermal Gravimetric Analysis

Isothermal reduction in thermogravimetric analysis (TGA) experiments was conducted using approximately 20 mg catalyst samples in a simultaneous TGA/DTA apparatus (TA Instruments, Model SDT 2960). The catalyst sample was purged with helium (40 cm<sup>3</sup>/min) and temperature was ramped at a rate of 5°C/min from room temperature to a desired reduction temperature (280°C) and then held at this temperature for 30 minutes to remove adsorbed moisture from the sample. The sample weight at the end of the heating period in helium is taken as a reference weight of the sample. After that, the flow was switched to pure H<sub>2</sub>, and weight loss of sample was recorded as a function of time. The observed weight loss is related to the degree of reduction of Fe<sub>2</sub>O<sub>3</sub>. The degree of reduction is calculated by dividing the observed weight loss with the theoretical weight loss corresponding to the complete reduction of Fe<sub>2</sub>O<sub>3</sub> to metallic Fe. Contribution from reduction of CuO to Cu has been neglected, whereas the other oxides in a sample are assumed to remain in the oxide form.

## Results and Discussion

Table 1 summarizes properties of support materials used to synthesize catalysts at TAMU. Surface areas and pore volumes of uncalcined (as received) supports were reported by suppliers (W. R. Grace - silica supports, Condea Vista- alumina supports) whereas particle density measurements and surface areas of calcined supports were made at the UNM.

Table 1. Selected Support Properties

Designation	Davison 952		Davison 948		Condea HP 14-150		Condea HP 14		Condea Vista B
Type	Silica gel			$\gamma$ -Alumina		Boehmite			
	uncalc.	uncalc.	calcined <sup>a</sup>	uncalc.	calcined <sup>a</sup>	uncalc.	calcined <sup>a</sup>	uncalc.	
Density (g/cm <sup>3</sup> )	2.22	2.09	2.08	3.07	3.07	2.71	2.68	2.24	
Pore volume (cm <sup>3</sup> /g)	1.61	1.62		0.97		0.94		0.47	
Surface area (m <sup>2</sup> /g)	309	279	304	153	157	150	156	243	

<sup>a</sup> Calcined in air at 500°C for 5 hours

Condea HP 14 and HP 14-150 microspherical particles (prepared by spray drying)

Davison 952 and Condea Vista B were used as catalyst supports at TAMU during the DOE contract (DE-AC22-94PC93069) and their attrition properties were evaluated at the UNM. Silica supports have higher surface areas and pore volumes than the alumina supports used in our studies. Calcination at 500°C for 5 hours does not have significant effect on physical properties of support materials. Calcined (at 300°C for 5 hours) precipitated iron catalyst (100 Fe/3 Cu/4 K/16 SiO<sub>2</sub>) has the BET surface area of 291 m<sup>2</sup>/g and the pore volume of 0.43 cm<sup>3</sup>/g.

Reduction behavior of alumina and silica supported catalysts (100 Fe/8 Cu/8 K, 20 wt% Fe) prepared by aqueous impregnation is shown in Figure 1. As can be seen from this figure reducibility of iron decreases in the order: SiO<sub>2</sub> >  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (HP 14-150 uncalcined) >  $\gamma$ -alumina (HP 14-150 calcined) > Boehmite Al<sub>2</sub>O<sub>3</sub> (HP 14 calcined). Reduction of iron is complete after about 3 hours with the silica supported catalyst, and nearly complete (95 % reduction) with uncalcined HP 14-150 supported catalyst after 8 hours. Final degree of reduction of iron on boehmite alumina type support (HP 14) was only 54 % after 8 hours.

The effect of preparation method (aqueous vs. organic impregnation) and promoters (unpromoted catalyst vs. 100 Fe/8 Cu/8 K, both with 20 wt% Fe loading) on the reduction behavior is shown in Figure 2. It can be seen that the presence of promoters (primarily Cu) improves reduction of iron regardless of the preparation method. Reducibility of iron was improved with organic impregnation for the unpromoted catalyst, whereas in the presence of promoters the rate of reduction was slightly higher with the catalyst prepared by aqueous impregnation (up to 6 hours). Calculated degrees of reduction with promoted silica catalysts in Figures 1 and 2 exceed 100 % after 3-4 hours of reduction, due to experimental errors in measured weights and/or catalyst compositions.

Samples of synthesized catalysts, as well as samples withdrawn from a stirred tank slurry reactor tests (under both reactive and non-reactive conditions) were sent to our collaborators at the UNM and BYU for characterization studies by SEM/TEM, XRD and/or Mössbauer spectroscopy. Results from these characterization studies can be found in sections of the report prepared by the UNM and BYU.

### *Conclusions*

Several catalysts were prepared by aqueous incipient wetness impregnation (IWI) of commercially available alumina (Condea HP 14 and Condea HP 14-150) and silica (Davison 948) supports. All synthesized catalysts had iron loading of 20 wt%. Copper (Cu) and potassium (K) were used as standard promoters, in the following proportions relative to iron: 100 Fe/8 Cu/8 K (in parts per weight), which corresponds to 1.6 wt% loading for each of the two promoters. With the Davison 948 silica support catalysts were prepared by both aqueous and organic (methanol as solvent) impregnation to study the effect of preparation procedure on catalytic performance. Also, Na was used as a promoter instead of K, for the catalyst prepared from methanol solution (organic IWI). Two unpromoted silica supported catalysts (20 wt% Fe loading) were synthesized from both aqueous and methanol solutions for catalytic studies of the effect of promoters on activity and selectivity.

Reduction behavior of synthesized catalysts was studied in a TGA unit using pure H<sub>2</sub> as reducing gas at 280°C. For promoted catalysts prepared from aqueous solutions reducibility of iron decreases in the order: SiO<sub>2</sub> >  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (HP 14-150 uncalcined) >  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (HP 14-150 calcined) > Boehmite Al<sub>2</sub>O<sub>3</sub> (HP 14 calcined). Presence of Cu improves reduction of iron regardless of the preparation method (aqueous vs. organic impregnation). Reducibility of iron was improved with organic impregnation for the unpromoted catalyst.

### **Task 3. Attrition Resistance Tests**

We have examined several commercially available silica and alumina supports (Table 1) to determine their suitability for preparing attrition-resistant Fe catalysts. Two types of tests were conducted to assess the attrition resistance of various support materials as well as that of a precipitated iron catalyst (100 Fe/3 Cu/4 K/16 SiO<sub>2</sub>). In ultrasonic fragmentation tests, conducted at the UNM, catalyst (or support) particles were subjected to ultrasound energy over different time periods, and particle size distribution was measured after different

exposures to ultrasonic fragmentation (Kalakkad et al., 1995; Pham et al., 1999, 2000). Attrition properties were also studied under reactive and nonreactive conditions in a stirred tank slurry reactor (STSR) at TAMU. Under non-reacting conditions, nitrogen was used as the feed gas, while under reacting F-T conditions; syngas was used as the feed gas. Slurry samples were withdrawn from the STSR and particle size distributions were subsequently measured at UNM after extraction of slurry liquid from the powder. A brief description of experimental procedures employed is provided here, followed by description of results from tests with supports and catalysts conducted at TAMU. More comprehensive information on attrition testing, including a wider range of supports and catalysts can be found in a section of the report prepared by the UNM.

## *Experimental*

### 3.1 Ultrasound Fragmentation Testing

In a typical run, 1 g of catalyst or support was added to 50 ml of a 0.05 wt.% sodium hexametaphosphate solution which was used as a dispersing agent. A Micromeritics Sedigraph 5100 analyzer was used to measure the particle size distribution at time 0 min. The suspension was then subjected to ultrasonic energy at an amplitude setting of 20 (100 W) at 5 min intervals using a Tekmar 501 ultrasonic disrupter equipped with a V1A horn and a 12.7 mm (1/2") probe tip (20 kHz  $\pm$  50 Hz). After different extents of ultrasonic irradiation, the particle size distribution was analyzed to detect the mode of particle break-up.

### 3.2 Attrition Testing in a Stirred Tank Slurry Reactor

Experiments were conducted in a 1 dm<sup>3</sup> reactor (Autoclave Engineers, Erie, Pennsylvania). A standard six-blade turbine impeller of 3.2 cm in diameter and a stirrer speed of 1200 rpm were used in all experiments. In a typical experiment the reactor was charged with 25 g of support (or catalyst) dispersed in 450-470 g of Durasyn-164 (hydrogenated 1-decene homopolymer). Nitrogen at 260°C, 1.48 MPa (200 psig) and 3 NI/g/h was used as the feed gas in experiments under nonreactive conditions (NI = Normal liter at standard temperature, 0°C, and pressure, 1 bar). Slurry samples were withdrawn from the STSR at 0, 8, 24 and 168 h of stirring, and Durasyn-164 was removed by filtration aided by addition of a commercial solvent Varsol (mixture of liquid hydrocarbons and oxygenates). Washing with Varsol was done to remove Durasyn-164 (or wax in the case of experiments under reactive conditions) from catalyst (support) porous structure. Dry particles were sent to UNM for particle size distribution measurements (Micromeritics Sedigraph 5100 analyzer).

Slurry samples were also withdrawn from the STSR during F-T synthesis at 260°C, 1.48-2.17 MPa, 0.8-1.2 NI/g-cat/h using syngas feed with H<sub>2</sub>/CO molar feed ratio of ~2/3. After removal of slurry liquid and wax from pores a dry catalyst powder was shipped to UNM for particle size distribution measurements. This provides information on the combined effect of phase transformations, which occur during F-T synthesis and physical break-up of particles (due to particle collisions and shearing effects), on attrition properties of the catalyst.

## *Results and Discussion*

Figure 3 shows a cumulative particle size distribution plot of mass finer (%) vs. equivalent spherical diameters for representative support materials used for preparation of catalysts by IWI at TAMU, and of precipitated iron catalyst (uncalcined form) during ultrasound fragmentation tests. Fracture of particles is seen for two alumina supports (Figs. 3a and 3b), as indicated by the shift in curves to the right with time, i.e., towards smaller size particles. However, more fine particles are seen with Condea HP 14-150 ( $\gamma$ -alumina) than with Condea HP 14 (boehmite) during ultrasonic irradiation. Nevertheless, very little generation of fine particles due to erosion (as indicated by an increase in the percentage of fines for a particular particle size) is seen below 6  $\mu\text{m}$  for Condea HP 14 and 3  $\mu\text{m}$  for Condea HP 14-150. The median particle sizes for Condea HP 14 and HP 140/150 are 37  $\mu\text{m}$  and 32  $\mu\text{m}$ , respectively. SEM images (not shown) showed that Condea HP 14 and HP 14-150 particles are roughly spherical in shape, suggesting that these alumina particles came from a spray-drying process. For Davison 948 (Figure 3c) very little attrition of particles due to fracture is seen after 25 min of ultrasonic irradiation. The median particle size is 34  $\mu\text{m}$ . There is very little generation of fine particles due to erosion below 6  $\mu\text{m}$ . SEM images showed that Davison 948 particles are roughly spherical. Uncalcined precipitated iron catalyst (100 Fe/3 Cu/4 K/16 SiO<sub>2</sub>) showed very little fragmentation and erosion during ultrasound fragmentation test (Figure 3d). Similar results (not shown) were obtained after calcination at 300°C for 5 h. Precipitated catalyst particles are irregularly shaped (as indicated by SEM) and its median size was 13  $\mu\text{m}$  (uncalcined catalyst) and 16  $\mu\text{m}$  (calcined catalyst).

Results from attrition tests in a STSR under non-reacting conditions are shown in Figure 4. In this case, Condea HP 14 and HP 14-150 supports do not show significant fracture, but there is generation of fine particles in the 1 – 10  $\mu\text{m}$  range after use in the STSR after 8 h of stirring (Figures 4a and 4b). The amount of fines does not increase with time (up to 168 h). Davison 948 silica shows some fragmentation (distribution shifts to the right) after 8 hours in the STSR (Fig. 4c). Some erosion is evident after 24 and 168 hours of testing, but the production of fines is lower in comparison to the two alumina supports. The erosion of supports was more pronounced during the STSR tests of supported catalysts than during the ultrasonic irradiation tests.

Precipitated TAMU catalyst (100 Fe/3 Cu/4 K/16 SiO<sub>2</sub>) calcined at 300°C for 5 hours showed very little change in particle size distribution (high attrition strength) during 161 hours of testing in N<sub>2</sub> atmosphere (Figure 4d). Very little erosion is observed in 5-6  $\mu\text{m}$  range. After 161 h of testing in N<sub>2</sub> the catalyst was reduced in pure CO at 0.8 MPa (100 psig), 280°C and space velocity of 3 NI/g-cat/h for 8 hours. Following the reduction with CO the flow was switched to N<sub>2</sub> at 260°C, 1.48 MPa and 3 NI/g-cat/h to assess the attrition resistance of the CO reduced catalyst. Particle size distribution (PSD) determined by Sedigraph analyzer shows shift to the left, which is indicative of particle agglomeration (the fraction of particles finer than a given particle size decreases relative to TOS = 161 hours). This is believed to be due to experimental artifacts and errors. For example, this could result from a loss of small particles during slurry filtration and/or errors in particle density measurements. The same trend, i.e. shift of PSD to the left, was also observed with some of the supported catalyst samples withdrawn from the STSR during F-T synthesis (Figure 5).

Figure 5 shows results of PSD measurements of catalyst samples withdrawn from the STSR during F-T synthesis reaction studies. The first sample (TOS = 0 hr) was withdrawn from the reactor prior to CO reduction (calcined catalyst in oxide form). All catalysts were reduced in CO at 280°C, 0.8 MPa and 3 NI/g-cat/h for 8 hours prior to introduction of syngas ( $H_2/CO = 2/3$ ). Initially, all catalysts were tested at 260°C, 1.48 MPa and 4 NI/g-Fe/h. In some runs the catalysts were also tested at 2.17 MPa (300 psig) and 5.9 NI/g-Fe/h.

PSD shifted to the left with time in all cases, which is indicative of particle agglomeration. For 20% Fe/HP 14  $Al_2O_3$  catalyst (run SB-1250), this trend was observed for particles greater than 10  $\mu m$ , whereas for particles smaller than 10  $\mu m$  there was apparently some erosion with time (Figure 5a). Similar, but less pronounced, trend was observed in run SB-1640 with 20% Fe/uncalcined HP 14-150  $Al_2O_3$  catalyst (Figure 5b). On the other hand, for the silica supported catalyst (run SA-1090) and precipitated TAMU catalyst (run SB-0470) the fraction of smaller particles decreased with time for all particle size ranges (Figures 5c and 5d). It should be noted that in run SB-0470 the catalyst was not exposed to syngas during the entire test. During first 161 hours the catalyst in oxide form was first exposed to  $N_2$  gas (Period 1). After reduction in CO for 8 hours the carburized catalyst was tested in  $N_2$  again between 170 and 282 hours (Period 2). Results from PSD measurements during these two periods (0-281 hours) are shown in Figure 4. Finally, between 284 and 405 hours on stream (Period 3), the catalyst was exposed to synthesis gas ( $H_2/CO = 2/3$ ) at 260°C, 1.48 MPa and 2.3 NI/g-cat/h.

### *Conclusions*

The attrition behavior of several commercially available oxide supports and precipitated TAMU catalyst (100 Fe/3 Cu/4 K/16  $SiO_2$ ) was studied by ultrasound fragmentation and testing in STSR. The ultrasonic fragmentation method requires a small sample amount and is much quicker than actual testing in a reactor. Condea HP 14 boehmite alumina, Condea HP 14-150  $\gamma-Al_2O_3$  and Davison 948 silica appear to be prepared by spray drying, since they have nearly spherical particles. Alumina supports showed evidence of significant fracture, and some break-up due to erosion, during the ultrasonic fragmentation tests. Davison 948 silica and precipitated TAMU catalyst were resistant to ultrasonic fragmentation, and showed very little erosion. Several of these supports were tested for long term periods in a stirred tank reactor under conditions simulating F-T synthesis reaction conditions. We found that the STSR testing may be more severe to erosion in terms of its effect on the break-up of the support particles. However, both the alumina and Davison 948 silica supports were found to be sufficiently strong for testing under reaction conditions. In the next step, we synthesized Fe F-T catalysts with 20 wt% loading on Condea alumina supports (HP 14 and HP 14-150) and Davison 948 silica support. These catalysts were then tested under actual F-T reaction conditions for extended times. With the alumina supported catalysts fine particles in the size range of 1-10  $\mu m$  were generated (about 15 wt%). The silica supported catalyst (Davison 948) appears to be more resistant to erosion than the alumina supports. Attrition resistance behavior of the precipitated TAMU catalyst was comparable to or better than that of Davison 948 silica in both types of tests (ultrasound fragmentation and STSR tests). Its attrition resistance could be further improved by preparing the catalyst in form of micro-spherical particles (e.g. by spray drying).

#### Task 4. Catalyst Testing and Data Analysis

Catalysts synthesized in Task 2 were tested in a stirred tank slurry reactor (STSR) to determine their activity, selectivity and stability during F-T synthesis. A complete list of tests conducted and catalysts employed is given in Table 2.

Table 2. Catalysts tested and reaction conditions

Run #	Catalyst/Support*	Preparation	Test conditions/ Hours
SB-0470	100 Fe/3 Cu/4 K/16 SiO <sub>2</sub>	Precipitation	Baseline (0-103 hrs) <sup>b</sup>
SA-1090	20% Fe/Davison 948 SiO <sub>2</sub>	Aqueous IWI	Baseline (0-113 hrs) High P <sup>c</sup> (114-235 hrs)
SB-1250	20% Fe/HP 14 Al <sub>2</sub> O <sub>3</sub>	Aqueous IWI	Baseline (0-160 hrs)
SA-1380	20% Fe/HP 14-150 Al <sub>2</sub> O <sub>3</sub>	Aqueous IWI	Baseline (0-113 hrs) High P <sup>c</sup> (114-263 hrs)
SB-1640	20% Fe/HP 14-150 Al <sub>2</sub> O <sub>3</sub> (uncalcined support)	Aqueous IWI	Baseline (0-165 hrs) High P <sup>c</sup> (166-236 hrs)
SA-1780	20% Fe/Davison 948 SiO <sub>2</sub>	Organic IWI	High SV <sup>d</sup> (0-53 hrs) Baseline (54-195 hrs) High P <sup>c</sup> (196-318 hrs)
SA-2450	20% Fe/Davison 948 SiO <sub>2</sub> (unpromoted)	Aqueous IWI	Baseline (0-130 hrs) Low SV <sup>e</sup> (131-240) High P <sup>f</sup> (242-315 hrs)
SA-3210	20% Fe/Davison 948 SiO <sub>2</sub> (unpromoted)	Organic IWI	Baseline (0-119 hrs) High P <sup>c</sup> (120-169 hrs)
SB-1221	20% Fe/Davison 948 SiO <sub>2</sub> (Na promoted) <sup>a</sup>	Organic IWI	Baseline (0-160 hrs)

Footnotes for Table 2:

\*All supports were calcined at 500°C for 5 hours unless indicated otherwise. All supported catalysts were promoted with both Cu and K (100 Fe/8 Cu/8 K in pbw) unless indicated otherwise. Unpromoted catalyst contains only Fe.

<sup>a</sup> This catalyst contains Na instead of K as an alkali promoter (100 Fe/8 Cu/8 Na in pbw).

<sup>b</sup> Baseline conditions: 260°C, H<sub>2</sub>/CO = 2/3, P = 1.48 MPa, SV = 4.0 NI/g-Fe/h.

<sup>c</sup> High P conditions: 260°C, H<sub>2</sub>/CO = 2/3, P = 2.17 MPa, SV = 5.9 NI/g-Fe/h.

<sup>d</sup> High SV conditions: 260°C, H<sub>2</sub>/CO = 2/3, P = 1.48 MPa, SV = 6.0 NI/g-Fe/h.

<sup>e</sup> Low SV conditions: 260°C, H<sub>2</sub>/CO = 2/3, P = 1.48 MPa, SV = 2.1 NI/g-Fe/h.

<sup>f</sup> High P conditions: 260°C, H<sub>2</sub>/CO = 2/3, P = 2.17 MPa, SV = 3.1 NI/g-Fe/h.

The following coding system was used to designate experimental tests. Two letter prefix (SA or SB) refers to the reactor unit used for the test (S = slurry reactor; A or B - reactor unit). The first three digits refer to the day of the year corresponding to the start of the run, whereas fourth digit corresponds to the last digit in the year of the start date (e.g. 0 for 2000. 1 for 2001).

## *Experimental*

A detailed description of our stirred tank slurry reactor and product analysis systems used in this study was provided elsewhere (Bukur et al., 1990b, 1994; Zimmerman and Bukur, 1990). Briefly, experiments were conducted in a 1 dm<sup>3</sup> reactor (Autoclave Engineers, Erie, Pennsylvania). A standard six-blade turbine impeller of 3.2 cm in diameter and a stirrer speed of 1200 rpm were used in all experiments. The feed gas flow rate was adjusted with a mass flow controller and passed through a series of oxygen removal, alumina and activated charcoal traps to remove trace impurities. The feed was preheated before entering the reactor. After leaving the reactor, the exit gas passed through a series of high and low (ambient) pressure traps to condense liquid products.

During mass balance periods liquid products were allowed to accumulate in high and low pressure mass balance traps, and their mass was recorded at the conclusion of the mass balance period. After the startup, and following any change in process conditions, the reactor was allowed to operate undisturbed for 20 - 40 hours in order to achieve steady conditions before the next mass balance was performed. Liquid products, collected in a low pressure ice trap, were analyzed by gas chromatography. The reactants and noncondensable products leaving the ice traps were analyzed on an on-line GC (Carle AGC 400, Tulsa, Oklahoma) equipped with multiple columns and both flame ionization and thermal conductivity detectors.

Typically, the reactor was loaded with 20-25 g of catalyst and 420-460 g of start-up liquid (Durasyn 164). After pressure testing, the temperature was increased to 150°C at 120°C/h in flowing N<sub>2</sub> (3 NI/g-cat/h) and held at 150°C for 2 hours. Then, pressure was increased to 0.78 MPa (100 psig) and temperature to 280°C at 65°C/h, followed by reduction at these conditions in CO (3 NI/g-cat/h) for 8 h (12 h in run SA-1780). After cooling to 260°C in N<sub>2</sub>, the pressure was increased to 1.48 MPa (200 psig) and the feed switched to syngas with a H<sub>2</sub>/CO ratio of 0.67 at a gas space velocity (SV) of 4 NI/g-Fe/h (baseline process conditions). After 5-8 days on stream at the baseline conditions, the pressure was increased to 2.17 MPa (300 psig), while the space velocity was adjusted to 5.9 NI/g-Fe/h to give the same residence time in the reactor. In some tests (SA-1780 and SA-2450) different process conditions were employed as shown in Table 2. However, all catalysts were tested at the baseline process conditions for comparison purposes.

## *Results and Discussion*

### 4.1 Activity and Selectivity Definitions

Before describing results from stirred tank slurry reactor tests we provide definitions of activity and selectivity used in this report.

$$(\text{H}_2+\text{CO}) \text{ conversion (\%)} = 100 \times ((\text{Moles of H}_2+\text{CO})_{\text{in}} - (\text{Moles of H}_2+\text{CO})_{\text{out}})/(\text{Moles of H}_2+ \text{CO})_{\text{in}}$$



Apparent reaction rate constant,  $k$  (mmol (H<sub>2</sub>+CO) converted/g-Fe/h/MPa), was calculated assuming that the rate of disappearance of (H<sub>2</sub>+CO) has a first order dependence on hydrogen partial pressure:

$$k = \frac{1000 \times SV \times X_{H_2+CO}}{22.4 \times P_{H_2} \times w_{Fe}}$$

where:  $SV$  = gas space velocity (NI/g-cat/h);  $X_{H_2+CO}$  = syngas conversion (-);  $P_{H_2}$  = partial pressure of hydrogen (MPa);  $w_{Fe}$  = mass fraction of iron in the catalyst (-).

$$\text{CO}_2 \text{ selectivity (\%)} = 100 \times \frac{(n_{CO_2})_{out}}{(n_{CO})_{in} - (n_{CO})_{out}}$$

Hydrocarbon selectivity on carbon atom basis is calculated from:

$$S_{ij}(\%) = \frac{100 \times (in_{ij})}{(n_{CO})_{in} - (n_{CO})_{out} - (n_{CO_2})_{out}}$$

where:  $S_{ij}$  is the selectivity of hydrocarbon species  $j$  containing  $i$  carbon atoms,  $n_{ij}$  is molar flow of compound  $j$  in the gas phase,  $(n_{CO})_{in}$  and  $(n_{CO})_{out}$  are molar flow rates of CO in and out of the reactor, and  $(n_{CO_2})_{out}$  is the molar flow rate of carbon dioxide out of the reactor. The above formulas assume that there is no carbon dioxide in the feed.

Olefin selectivities (contents) are calculated as:

$$\text{1-olefin selectivity (\%)} = 100 \times \frac{\text{1-olefin}}{\text{1-olefin} + \text{2-olefin}}$$

$$\text{2-olefin selectivity (\%)} = 100 \times \frac{\text{2-olefin}}{\text{1-olefin} + \text{2-olefin}}$$

$$\text{Total olefin selectivity (\%)} = 100 \times \frac{\text{linear olefins}}{\text{n-paraffin} + \text{linear olefins}}$$

#### 4.2 Run SB-0470 with Precipitated Iron Catalyst 100 Fe/3 Cu/4 K/16 SiO<sub>2</sub>

Some of precipitated iron F-T catalysts (Fe/Cu/K/SiO<sub>2</sub>) synthesized and tested at TAMU, under DOE sponsorship, have excellent performance characteristics. They are more active than iron catalysts developed by Mobil (Kuo, 1985) and Rheinpreussen (Kölbel et al., 1955) while exhibiting high syngas conversion and selectivity to liquid and wax hydrocarbons. One of the best catalysts developed at TAMU has a nominal composition of 100 Fe/3 Cu/4 K/16 SiO<sub>2</sub>.

Performance characteristics of this catalyst from tests in a STSR are as follows (Bukur et al., 1994, 1998, 1999a; Bukur 1999b):

- Syngas conversion: ~ 80 %
- Catalyst productivity: 0.86 g-HC/g-Fe·h (at 2.17 MPa and 260°C)
- Low methane selectivity: ~ 3 wt% (2.5 % on carbon atom basis)
- $\alpha = 0.92-0.95$  (high alpha catalyst)
- C<sub>5</sub>+ selectivity: ~ 85% (high yield of liquid and hydrocarbon wax)
- No deactivation after 500 h of testing (runs SA-0946 and SA-2186)

However, even though TAMU's catalyst performance is excellent in terms of activity, selectivity and stability, there is a concern that the catalyst is structurally too weak and that it may disintegrate during F-T synthesis in a slurry bubble column reactor to form fine particles. The presence of fine particles causes problems with wax/catalyst separation by filtration or use of gravity settlers.

In order to test attrition properties of this catalyst, as well as to perform a test of our reactor system and analytical procedures, a run SB-0470 was conducted. The start-up procedure for this test was different than that employed in other tests. The entire test had four distinct periods, whose characteristics and purpose were as follows:

Period 1 - Attrition testing of calcined catalyst in N<sub>2</sub> atmosphere (260°C, 1.48 MPa, 3 NI/g-cat/h, TOS = 0-161 hours)

Period 2 - Reduction with CO at 280 °C, 0.78 MPa, 3 Ndm<sup>3</sup>/g-cat/h for 8 hours (162-170 h)

Period 3 - Attrition testing of reduced catalyst in N<sub>2</sub> atmosphere (260°C, 1.48 MPa, 3 NI/g-cat/h, 170-282 hours)

Period 4 - Fischer-Tropsch synthesis (260°C, 1.48 MPa, H<sub>2</sub>/CO=0.67, 2.3 NI/g-cat/h, 284-405 hours)

Catalyst samples were withdrawn from the reactor at: 0, 24, 161, 186, 281, 308 and 404 h on stream, and changes in particle size distribution with time were measured using a Sedigraph analyzer. Results from these measurements were described in the previous section of this report (Task 3. Attrition Resistance Tests) and it was found that this catalyst has good attrition properties (no fragmentation and very little erosion).

Figure 6 shows activity (syngas conversion), methane and C<sub>5</sub>+ hydrocarbon selectivity variation with time in runs SB-0470 and SA-0946. Run SA-0946 was conducted in 1986 (DOE Contract DE-AC-22-94PC93069) in the slurry reactor A using precipitated catalyst from a different preparation batch than that used in run SB-0470. Also, in run SA-0946 the catalyst was reduced with CO at the beginning of the test, and F-T synthesis was initiated immediately after the reduction, whereas in run SB-0470 the F-T synthesis was initiated after 274 hours of stirring in nitrogen. In spite of differences in operating procedure, reactor used, and preparation batch similar results were obtained in these two tests. Activity (measured by

syngas conversion) was essentially the same in both tests. After 30 hours on stream methane selectivity was somewhat lower and C<sub>5</sub>+ selectivity higher in run SB-0470. These two tests confirm reproducibility of catalyst preparation procedure, which was established previously (Bukur et al., 1998; Bukur 1999b) and demonstrate robustness of this catalyst.

#### 4.3 Tests with Alumina Supported Catalysts

Two types of alumina from Condea were used as supports: HP 14 (boehmite) and HP 14-150 ( $\gamma$ -alumina). The latter was used to prepare two different catalysts. In one case as received (uncalcined) support was impregnated with iron and promoter salts and the resulting catalyst was tested in run SB-1640, whereas the second catalyst was prepared by impregnation of the calcined support and tested in run SA-1380. Results from three tests with alumina supports at the baseline conditions (260°C, 1.48 MPa, 4 NI/g-Fe/h, H<sub>2</sub>/CO = 2/3) are shown in Figures 7 and 8.

Catalyst prepared by impregnation of calcined  $\gamma$ -alumina (SA-1380) was the most active (Figures 7a and 7b), whereas catalyst prepared by impregnation of HP 14 alumina (SB-1250) was the least active. Both of these catalysts deactivated with time, whereas catalyst obtained by impregnation of uncalcined  $\gamma$ -alumina (SB-1640) was fairly stable during 165 hours of testing at the baseline conditions. Carbon dioxide selectivity is a measure of the extent of water-gas-shift (WGS) reaction, and 50% selectivity corresponds to complete conversion of water produced in F-T synthesis reaction (primary reaction step) to CO<sub>2</sub>. The extent of WGS reaction follows the catalyst F-T activity (Figure 7c); i.e. the catalyst with the highest F-T activity has the highest extent of the WGS reaction.

Methane selectivity was the least and C<sub>5</sub>+ selectivity the highest in run SA-1380 (Figure 8). Methane and C<sub>5</sub>+ selectivities in tests SB-1250 and SB-1640 were similar.

#### 4.4 Effect of Support Type (Silica vs. $\gamma$ -Alumina)

Results from tests with the calcined  $\gamma$ -alumina supported catalyst (SB-1380) and the silica supported catalyst (SA-1090) are shown in Figures 9 to 11. Both catalysts were prepared by aqueous impregnation (Table 2).

Figure 9 shows that the alumina supported catalyst was more active during testing at the baseline conditions (P = 1.48 MPa), with syngas conversion decreasing from 70% initially to 60% after 100 h on stream. The silica supported catalyst also deactivated during this time period and syngas conversion decreased from 60% initially to 50% at 100 h. After increasing pressure to 2.17 MPa and gas space velocity (see Table 2) the alumina supported catalyst deactivated rapidly initially and then more slowly reaching 40% conversion at 280 h on stream, whereas the silica supported catalyst did not show any further deactivation. CO<sub>2</sub> selectivity was similar for the two catalysts (Figure 9c) and was in the range 40-45%.

Methane and C<sub>5</sub>+ selectivities were more favorable on the alumina supported catalyst (Figure 10). Methane selectivity on the silica supported catalyst was fairly stable (7-8%), while in run SA-1380 it decreased from 6% initially to 4% after 200 h on stream (Figure 10a). As

expected C<sub>5</sub>+ selectivity in run SA-1380 exhibited the opposite trend, i.e. it increased from 72% to almost 80% (Figure 10b). C<sub>5</sub>+ selectivity in run SA-1090 was fairly stable, about 70%, decreasing somewhat after the increase in reaction pressure to 2.17 MPa.

Olefin selectivities are shown in Figure 11. The observed decrease in 1-olefin selectivity and increase in 2-olefin selectivity with increase in carbon number is due to secondary readsorption of 1-olefins and their subsequent conversion to n-paraffins (secondary hydrogenation) and to 2-olefins (secondary isomerization). Olefin selectivities were similar on both catalysts during testing at 1.48 MPa (baseline process conditions). Upon increasing reaction pressure to 2.17 MPa the 1-olefin selectivity increased and 2-olefin selectivity decreased in run SA-1380, whereas olefin selectivities did not change markedly with pressure in run SA-1090. The observed olefin selectivity trends in run SA-1380 may be explained in part by decrease in conversion, since lower conversion favors the primary reactions.

#### 4.5 Effect of Preparation Procedure (Aqueous vs. Organic Impregnation)

##### 4.5.1 Runs SA-1090 and SA-1780 with Promoted Silica Supported Catalysts

In an attempt to improve performance of the silica supported catalyst we used methanol as a solvent instead of water for incipient wetness impregnation (IWI). Two catalysts containing 20% Fe, and Cu and K as promoters (100 Fe/8 Cu/8 K in pbw) prepared by these two methods (see Task 2. Catalyst Synthesis and Characterization), were tested in runs SA-1090 (aqueous IWI) and SA-1780 (organic IWI). Reduction time in CO was 8 hours in run SA-1090 and 12 hours in run SA-1780. During first 53 hours on stream the catalyst in run SA-1780 was tested at a gas space velocity higher than the baseline space velocity (see Table 2) but these results are not shown here.

Initial catalyst activities in both tests were about the same as shown in Figure 12. Initially the syngas conversion was 60-63% and the apparent reaction rate constant about 330 mmol/g-Fe/MPa/h. Catalyst prepared from the organic solution did not deactivate during testing at the baseline conditions, whereas catalyst prepared from the aqueous solution deactivated with time and reached 46% syngas conversion at 150 hours. Catalyst activity was stable in both tests during testing at 2.17 MPa and gas space velocity of 5.9 NI/g-Fe/h. However, activity of the catalyst prepared by organic IWI method was higher. CO<sub>2</sub> selectivities in both tests were between 40% and 45%, and did not vary much with time (Figure 12c).

Methane selectivity (Figure 13a) in run SA-1090 was fairly constant (6-8%). Methane selectivity on the catalyst prepared from the organic solution was about 11% during testing at the baseline conditions, and then started to decrease during testing at 2.17 MPa reaching 9% at 300 hours. In run SA-1090 a maximum C<sub>5</sub>+ selectivity of 73% was reached after 60 h on stream, followed by a decrease to 65% at the end of the run (235 h). C<sub>5</sub>+ selectivity in run SA-1780 exhibited the opposite trend, i.e. an increase from 63% during testing at 1.48 MPa to 70% after increasing pressure to 2.17 MPa (Figure 13b). Total olefin selectivity did not vary much with time in both runs and average values are shown in Figure 13c. The catalyst

prepared from the organic solution had markedly lower olefin selectivity, indicative of a high degree of secondary olefin hydrogenation.

#### 4.5.2 Runs SA-2450 and SA-3210 with Unpromoted Silica Supported Catalysts

Two unpromoted (20% Fe/Davison 948 SiO<sub>2</sub>) catalysts were prepared in two different ways—impregnation from aqueous and from organic solution, and tested to further examine the effect of preparation procedure on the catalyst performance during F-T synthesis in the STSR. Results from tests SA-2450 (aqueous IWI) and SA-3210 (organic IWI) at the baseline reaction conditions are shown in Figures 14 and 15.

Catalyst prepared from methanol solution had higher activity than the catalyst prepared by aqueous impregnation of Davison 948 silica support, as reflected in higher syngas conversion and apparent reaction rate constant (Figures 14a and 14b). The apparent rate constant was about 50% higher in run SA-3210. Activity was fairly stable during 120-130 hours of testing at the baseline conditions. CO<sub>2</sub> selectivity was about 45% in run SA-3210 and 40% in run SA-2450 (Figure 14c). This difference is caused in part by differences in conversions between these two tests. Methane, C<sub>5</sub>+ and olefin selectivities were similar in both tests (Figure 15).

#### 4.6 Promoter Effects (Unpromoted vs. Cu and K Promoted) on Silica Supported Catalysts

Copper and potassium have been commonly used as promoters for precipitated iron F-T catalysts. The primary function of Cu promoter is to decrease the temperature required for reduction of iron oxides. This may result in higher catalyst F-T and WGS activity relative to unpromoted catalyst (Bukur et al., 1990c). Potassium promotion is known to increase: (1) the average molecular weight (chain length) of hydrocarbon products; (2) total olefin and 1-olefin selectivities; (3) the extent of WGS reaction; (4) carbon deposition rate and catalyst deactivation rate (Anderson, 1956; Dry, 1981; Arakawa and Bell, 1983; Bukur et al., 1990c). Also, the addition of K may have effect on rate of F-T synthesis (both an increase and decrease in reaction rate has been reported depending on the level of K promotion). Dry (1981, 1983, 1990) reported, based on studies conducted at Sasol, that potassium forms chemical compounds with silica and alumina supports, resulting in reduction of alkali promotional effect. Here we report results on the effect of combined Cu and K promotion on silica supported catalysts prepared by both aqueous and organic impregnation.

##### 4.6.1 Promoter Effects on Silica Supported Catalysts Prepared by Aqueous Impregnation

Results from tests with Cu+K promoted (run SA-1090) and unpromoted (run SA-2450) Fe catalysts, prepared by aqueous impregnation of Davison 948 silica, are shown in Figures 16 to 18. Initial activity of the promoted catalyst was slightly higher (Figures 16a and 16b) than that of the unpromoted catalyst, but the former deactivated faster with time and the activity trend was reversed after about 100 hours on stream. The unpromoted catalyst did not show signs of deactivation during 130 hours of testing at the baseline conditions. A discontinuity (drop in conversion and k values) at 90 h on stream is due to temporary drop in reaction

temperature. CO<sub>2</sub> selectivity of the promoted catalyst was slightly higher (Figure 16c), but in general both the F-T synthesis and WGS activity were similar on both catalysts.

Promoted catalyst has lower methane and higher C<sub>5</sub>+ selectivity than the unpromoted catalyst (Figure 17) which is consistent with the expected promotional effect of K. However, the promotional effect is rather small. The promoted catalyst has relatively high methane selectivity and low C<sub>5</sub>+ selectivity in comparison to TAMU's precipitated Fe catalyst (see Figure 6). The unpromoted catalyst had slightly lower 1-olefin selectivity and higher 2-olefin selectivity relative to the promoted catalyst (Figure 18), both of which are in qualitative agreement with the expected effect of K promotion on olefin selectivity.

#### 4.6.2 Promoter Effects on Silica Supported Catalysts Prepared by Methanol Impregnation

Comparison of activity and selectivity of the unpromoted (SA-3210) and Cu+K promoted (SA-1780) catalysts, prepared by organic impregnation of Davison 948 silica, is shown in Figures 19 and 20.

Both F-T catalyst activity (measured by syngas conversion) and WGS activity (measured by CO<sub>2</sub> selectivity) were similar on both catalysts (Figure 19). The unpromoted catalysts had lower methane and C<sub>5</sub>+ selectivity than the promoted catalyst (Figure 20). The expected lower methane selectivity with K promotion was not observed in this case, indicating that K promotion was not effective. 1-olefin selectivities were similar on both catalysts, whereas the unpromoted catalyst had higher 2-olefin selectivity (not shown).

#### 4.7 Effect of Alkali Promoter (Na vs. K as alkali promoter)

Since potassium promotion of the silica supported catalyst prepared from methanol solution was found to be ineffective in run SA-1780, we decided to investigate the effect of using sodium instead of K as an alkali promoter. Solubility of sodium nitrate in methanol is much higher than that of potassium salts, and this may result in a better dispersion of Na and improved contact with Fe. 20% Fe/Davison 948 SiO<sub>2</sub> catalyst containing Cu and Na as promoters (100 Fe/8 Cu/8 Na) was prepared as described on page 8 of this report, and tested at the baseline process conditions in run SB-1221. Results from runs SB-1221 and SA-1780 (100 Fe/8 Cu/8 K catalyst) are shown in Figures 21 and 22. The K promoted catalyst was initially (0-53 hours) tested at gas space velocity of 6 NL/g-Fe/h, but these results are not shown.

Activity of the Na promoted catalyst was lower than that of the K promoted catalyst (Figure 21). Syngas conversion on the K promoted catalyst was stable (61-63%), whereas the Na promoted catalyst deactivated with time, and conversion decreased from 53% initially to 46% at 150 h on stream. Similar initial CO<sub>2</sub> selectivities were obtained, but CO<sub>2</sub> selectivity on the Na decreased with time following the same trend as F-T activity.

Methane selectivity was similar on both catalysts (Figure 22a), but the K promoted catalyst had slightly higher C<sub>5</sub>+ selectivity (~64% vs. 60%) as shown in Figure 22b. Total olefin

selectivity was slightly lower on the Na promoted catalyst relative to the K promoted catalyst (Figure 22c).

### *Conclusions*

Results from tests with Cu and K promoted Fe catalysts prepared by aqueous IWI of supports, showed that calcined  $\gamma$ -alumina (HP 14-150) is a more promising support than boehmite alumina (HP 14) for F-T synthesis. Calcination of  $\gamma$ -alumina is an important step, and the catalyst prepared by IWI of calcined support (at 500°C for 5 hours) was superior to the one prepared by IWI of uncalcined (as received)  $\gamma$ -alumina support. Silica supported catalyst had lower initial activity and selectivity to C<sub>5+</sub> hydrocarbons, and higher methane selectivity than the calcined  $\gamma$ -alumina supported catalyst, but it deactivated less severely. Improvements in stability are needed for both silica and alumina supported catalysts.

With Cu and K promoted 20% Fe/SiO<sub>2</sub> catalysts, the catalyst prepared from methanol solution had better activity maintenance than the catalyst prepared from aqueous solution. However, the initial catalyst activity was the same for both catalysts. Hydrocarbon selectivity of the catalyst prepared by organic IWI was inferior (more methane and less C<sub>5+</sub> products) compared to the catalyst prepared by aqueous IWI during testing at the baseline process conditions (P = 1.48 MPa), but its selectivity improved during testing at higher reaction pressure (P = 2.17 MPa).

With unpromoted 20% Fe/SiO<sub>2</sub> catalysts, the catalyst prepared from methanol solution had higher activity than the catalyst prepared from aqueous solution. This is consistent with higher reducibility of the catalyst prepared by organic impregnation (Figure 2). Hydrocarbon selectivity on unpromoted catalysts was not affected by differences in preparation procedure.

The expected promotional effects of K (increase in molecular weight of hydrocarbon products, increased olefinicity, increase in WGS activity) were observed to a relatively small extent on the catalyst prepared by aqueous impregnation, but were less evident on the catalyst prepared by organic impregnation of Davison 948 silica support. F-T activity was not significantly affected by addition of Cu and K promoters, but the deactivation rate was higher on the promoted catalyst prepared by aqueous impregnation. Catalysts prepared by organic impregnation (both promoted and unpromoted) were more stable (low deactivation rate). The amount of K promoter used is rather high (8 parts per 100 parts of Fe on weight basis) compared to Fe precipitated catalysts, but its promotional effect was small. This is indicative of promoter-support interactions and/or decreased Fe-K contact. Substitution of K with Na (silica supported catalyst prepared by IWI from methanol solution) was found to result in inferior performance in terms of activity, selectivity and stability with time.

Silica and alumina supported catalysts produced significantly more methane (4-8 % on carbon atom basis) than the precipitated TAMU catalyst (~2.5 %). Also, both their activity and stability were inferior in comparison to that of the precipitated catalysts. Further work is needed to develop basic understanding of underlying causes for differences in the reaction behaviors and to synthesize improved supported Fe catalysts for slurry phase F-T synthesis.

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Ms. Patricia O'Dowd (graduate student) synthesized most of the catalysts used in this study. Mr. Alec Klinghoffer (graduate student) performed some of the attrition tests of supports under non-reactive conditions. Drs. Ketil Hanssen and Lech Nowicki evaluated catalyst performance in a stirred tank slurry reactor, performed attrition tests in a STSR, and synthesized some of the catalysts. Ms. Yanjun Wang helped with preparation of figures for this report. We had many valuable discussions with our collaborators at the UNM (Professor Datye and Dr. Hien Pham) and BYU (Professor Bartholomew and Mr. Jian Xu, graduate student).

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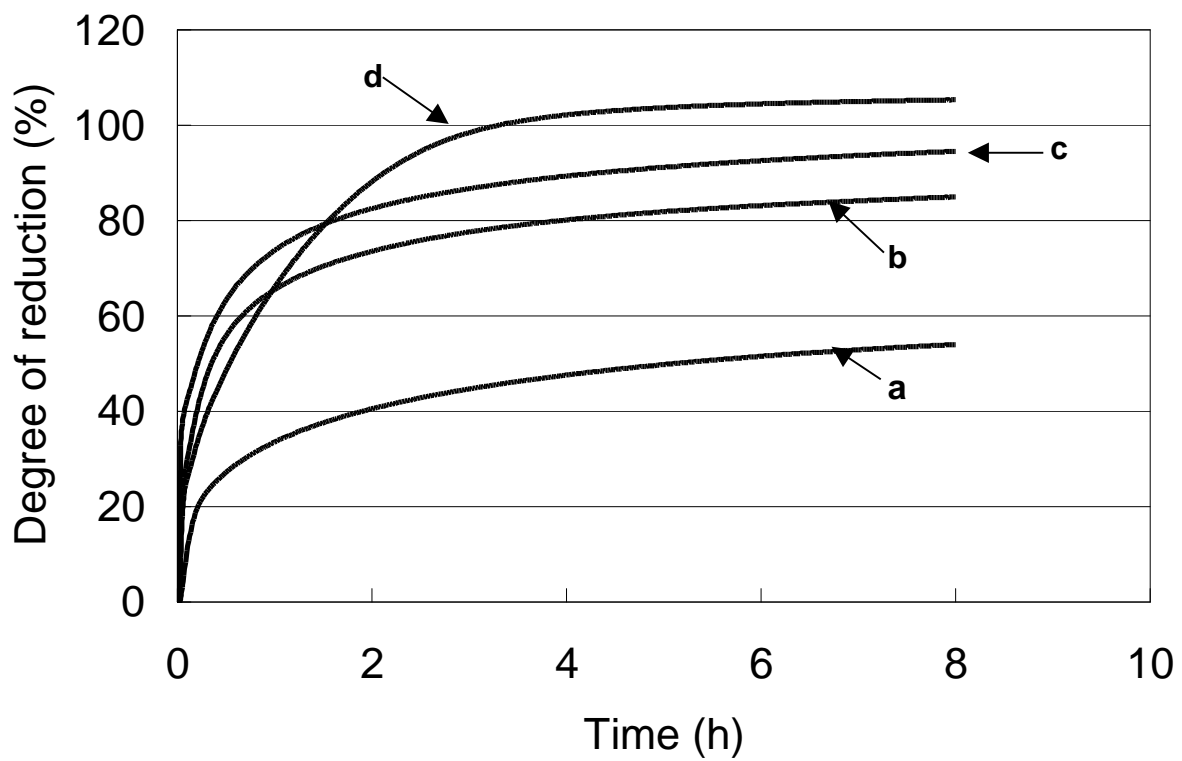


Figure 1 Isothermal reduction studies in pure H<sub>2</sub> with alumina and silica supported Fe catalysts: (a) HP 14 alumina; (b) HP 14-150 calcined  $\gamma$ -alumina; (c) HP 14-150 uncalcined  $\gamma$ -alumina; (d) Davison 948 silica.

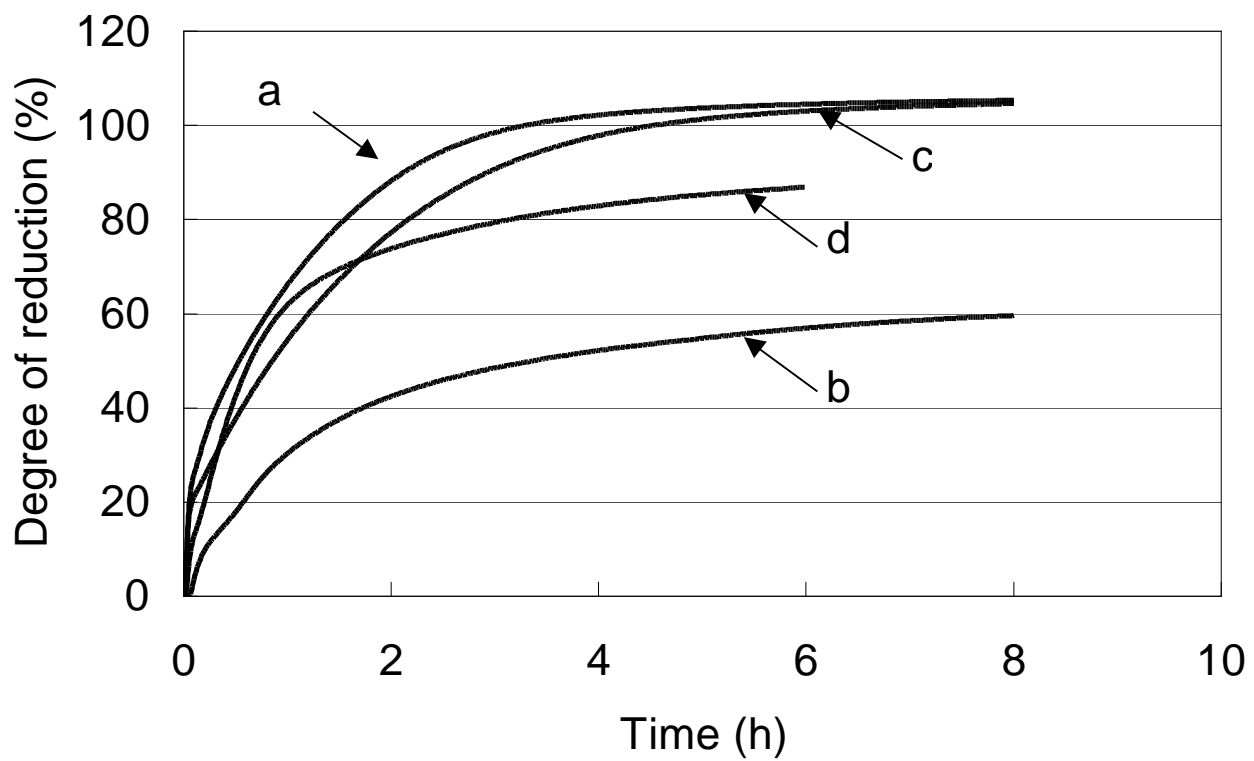


Figure 2 Effect of preparation procedure and promoters on reduction behavior of 20% Fe/Davison 948 silica catalysts: (a) K and Cu promoted (aq. impreg.); (b) Unpromoted (aq. impreg.); (c) K and Cu promoted (org. impreg.); (d) Unpromoted (org. impreg.).

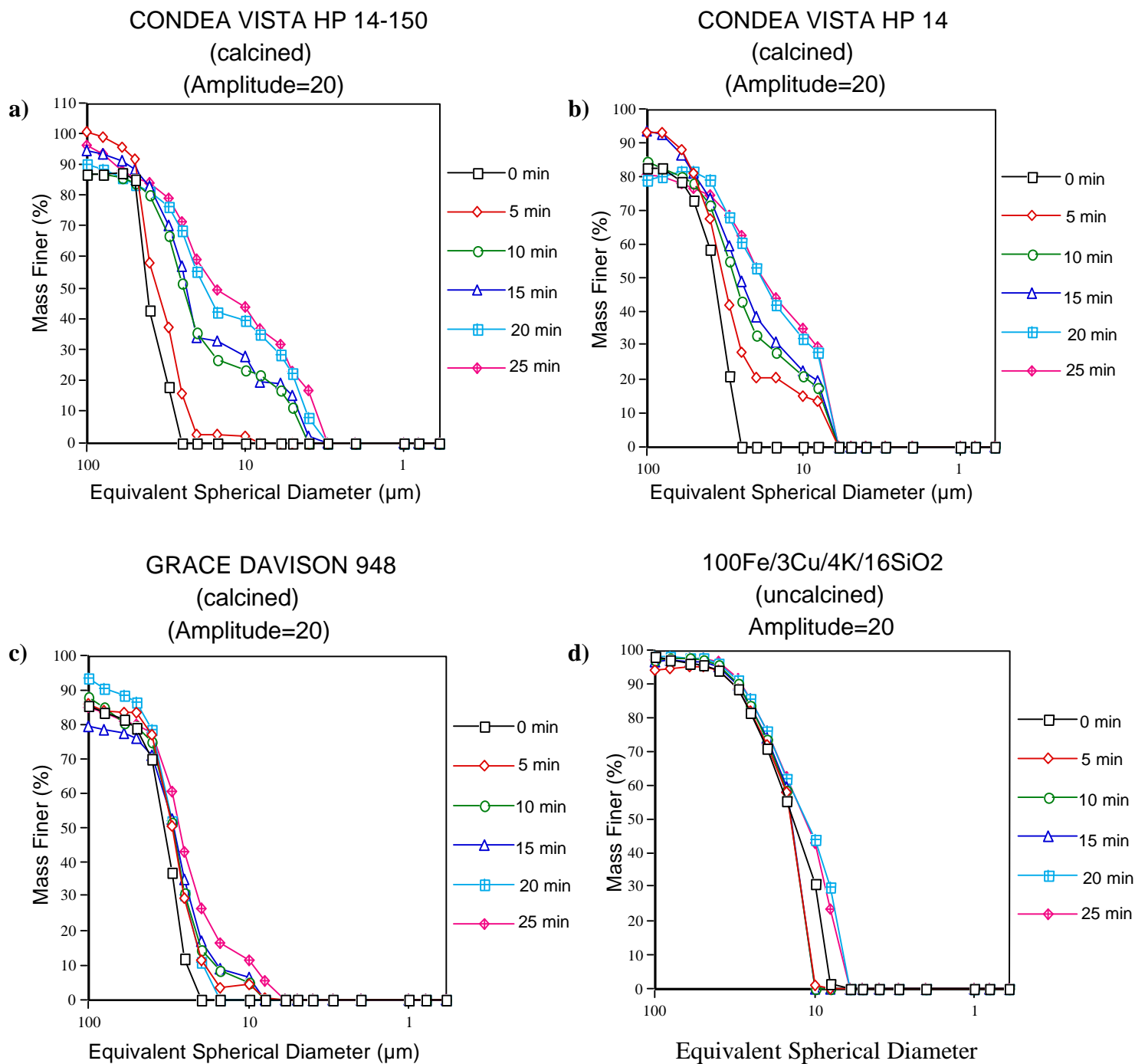


Figure 3. Sedigraph particle size distribution plots of these materials, performed under ultrasonic fragmentation tests. More fine particles are seen with Condea HP 14-150 (a) than with Condea HP 14 (b), during ultrasonic irradiation. For Davison 948 silica (c), very little attrition of particles due to fracture and erosion is seen after 25 min of ultrasonic irradiation. Similar results are found for the uncalcined precipitated iron catalyst (d).

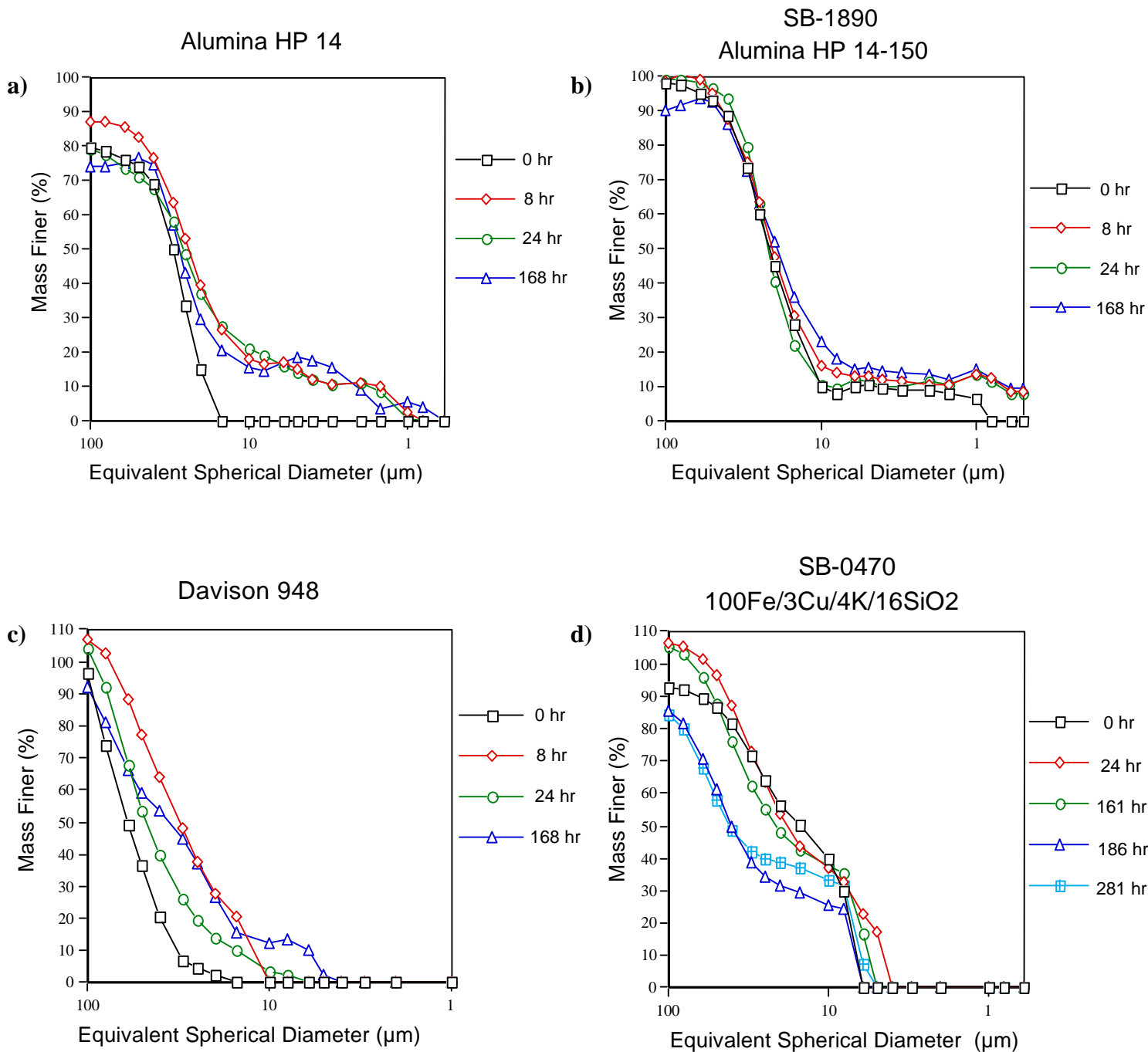


Figure 4. Sedigraph particle size distribution plots of these materials, performed in a STSR under non-reactive F-T conditions. Condea HP 14 (a) and HP 14-150 (b) do not show significant fracture, but there is generation of fine particles. For Davison 948 (c), there is some fragmentation after 8 h in the STSR. The precipitated catalyst (d) shows a change in particle size distribution when the reaction conditions were changed from inert atmosphere to CO reduction, after 161 h of testing.

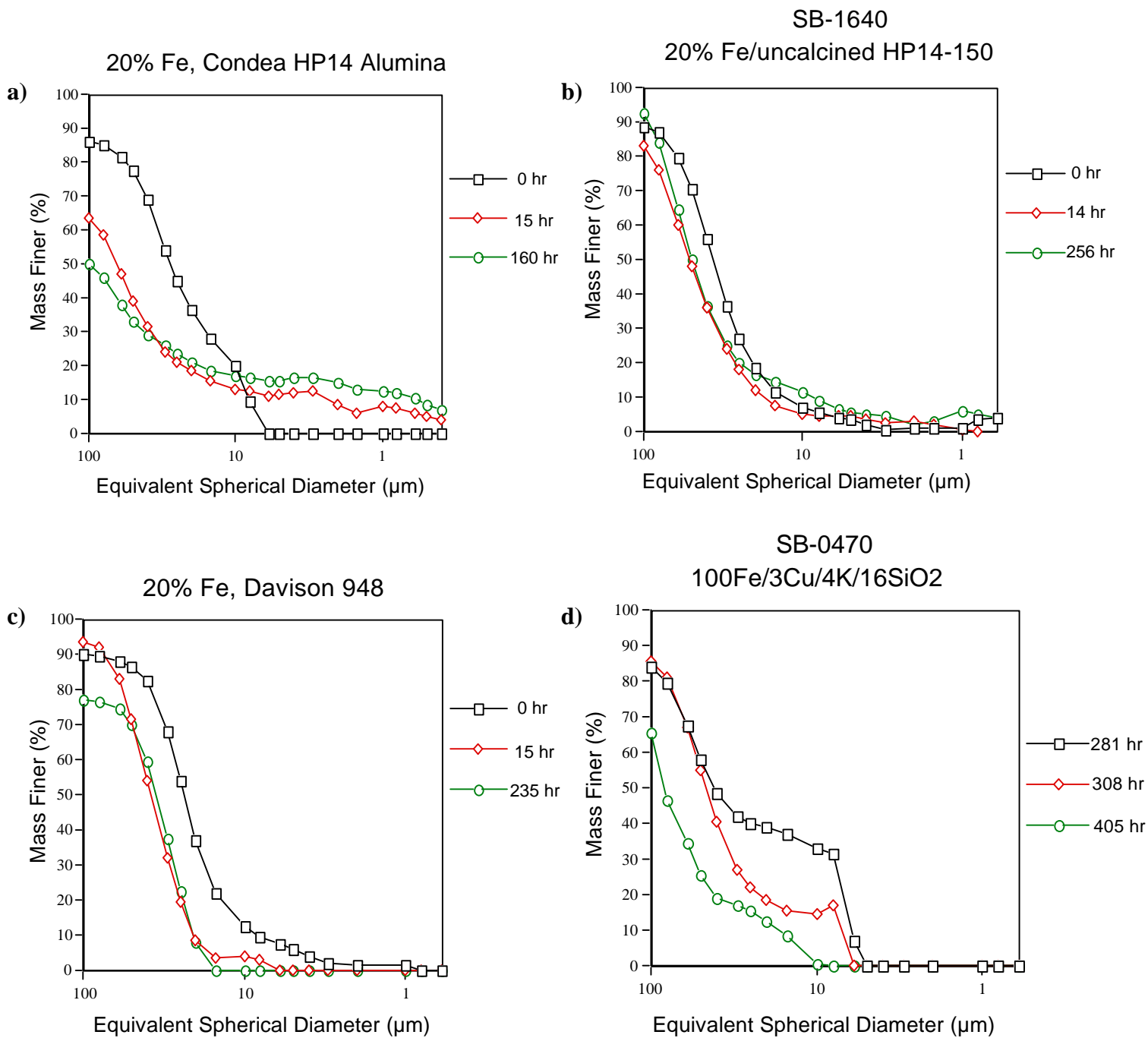


Figure 5. Sedigraph particle size distribution plots of these materials, performed in a STSR under F-T conditions. Particle size distribution shifted to the left with time in all cases (a-d), which is indicative of particle agglomeration. Note that for the precipitated catalyst (d), F-T reaction starts at 281 h, after non-reactive and CO reduction tests in the STSR.

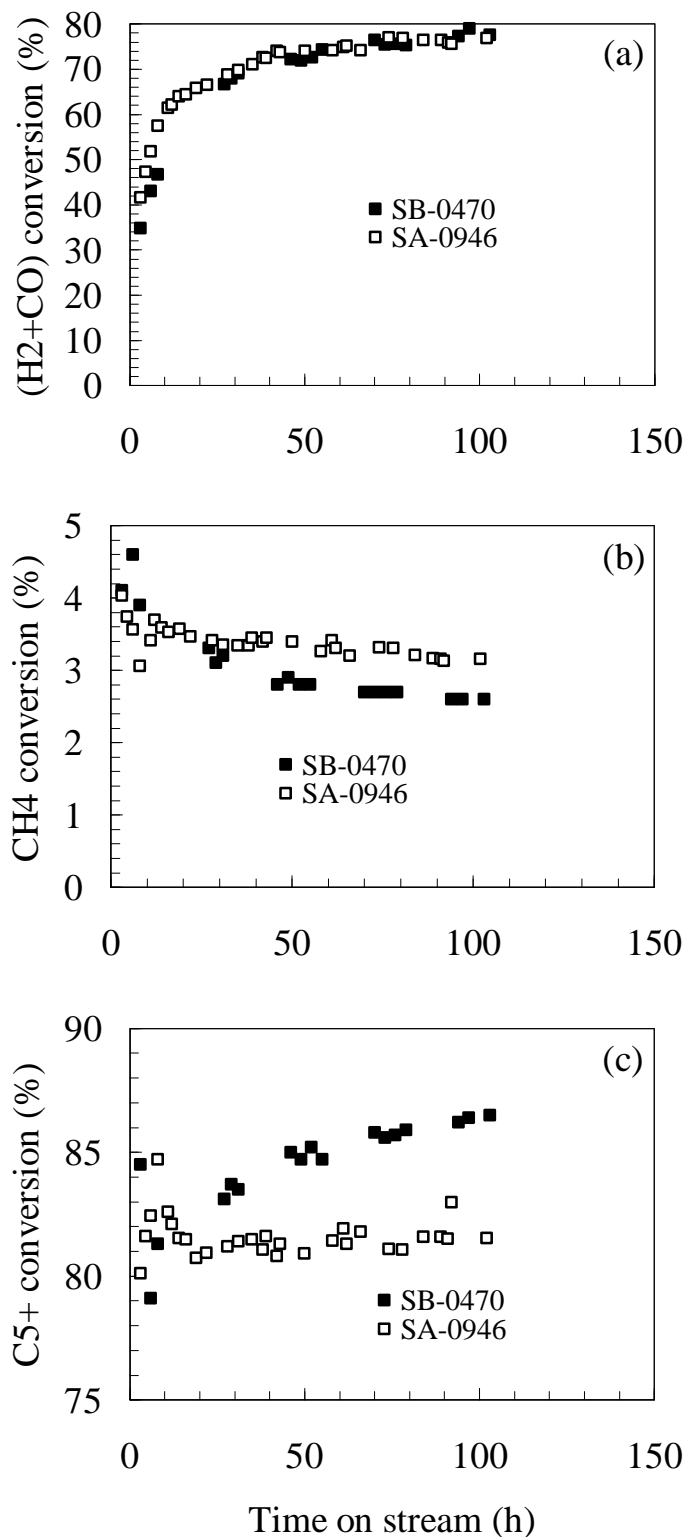


Figure 6 Activity and selectivity of precipitated 100 Fe/3 Cu/4 K/16 SiO<sub>2</sub> catalyst in stirred tank slurry reactor tests SA-0946 and SB-0470.

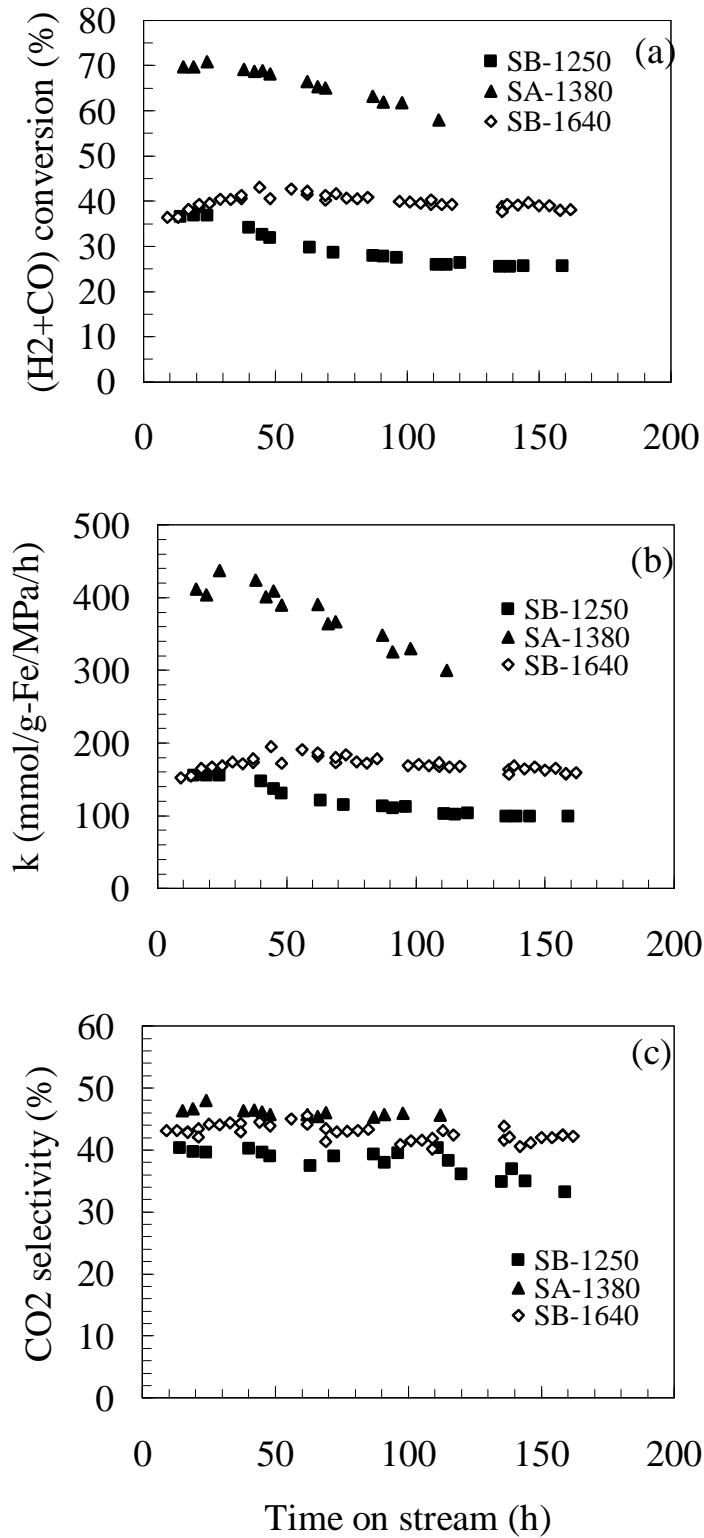


Figure 7 Slurry reactor tests of alumina supported catalysts - F-T and WGS activity (SB-1250 HP 14; SA-1380 HP 14-150 calcined; SB-1640 HP 14-150 uncalc.) Reaction conditions: 260°C, 1.48 MPa, 4.0 NI/g-Fe/h, H<sub>2</sub>/CO = 2/3



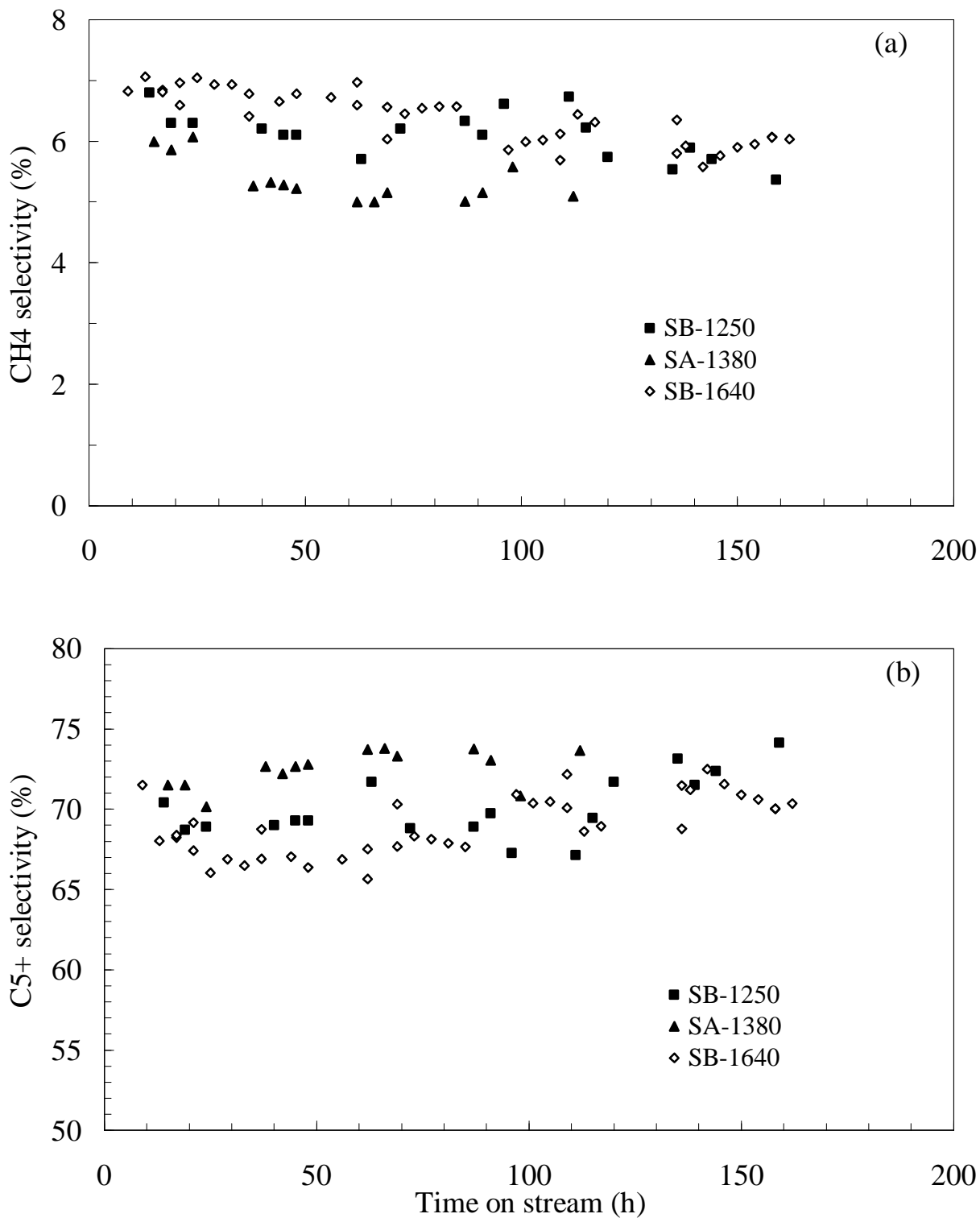


Figure 8 Slurry reactor tests of alumina supported catalysts - Product Selectivity (SB-1250 HP 14; SA-1380 HP 14-150 calcined; SB-1640 HP 14-150 uncalc.) Reaction conditions: 260°C, 1.48 MPa, 4.0 NI/g-Fe/h, H<sub>2</sub>/CO = 2/3

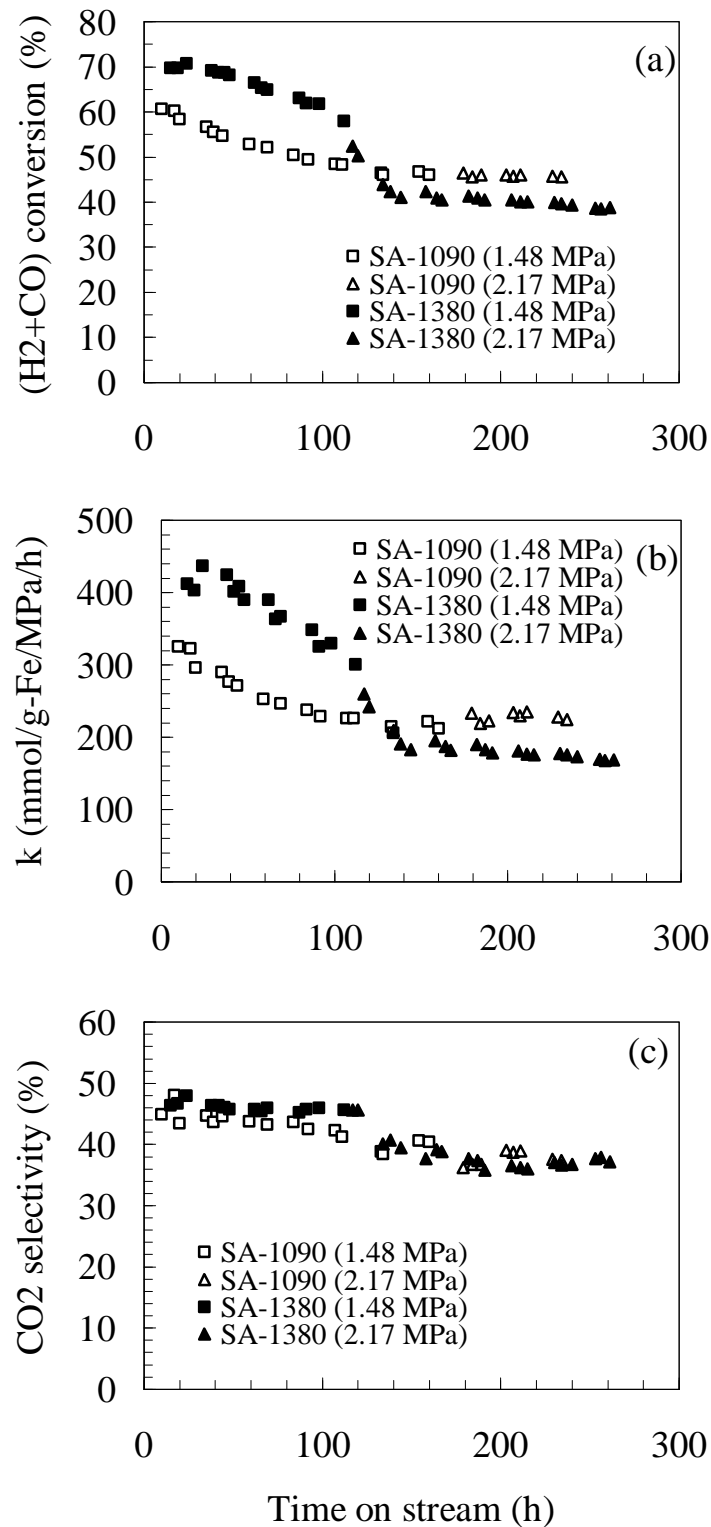


Figure 9 Effect of support type on F-T and WGS activity (SA-1380 HP 14-150 Al<sub>2</sub>O<sub>3</sub> (calcined); SA-1090 Davison 948 SiO<sub>2</sub>)  
 Process conditions: 1.48 MPa & 4.0 NI/g-Fe/h; or 2.17 MPa & 5.9 NI/g-Fe/h

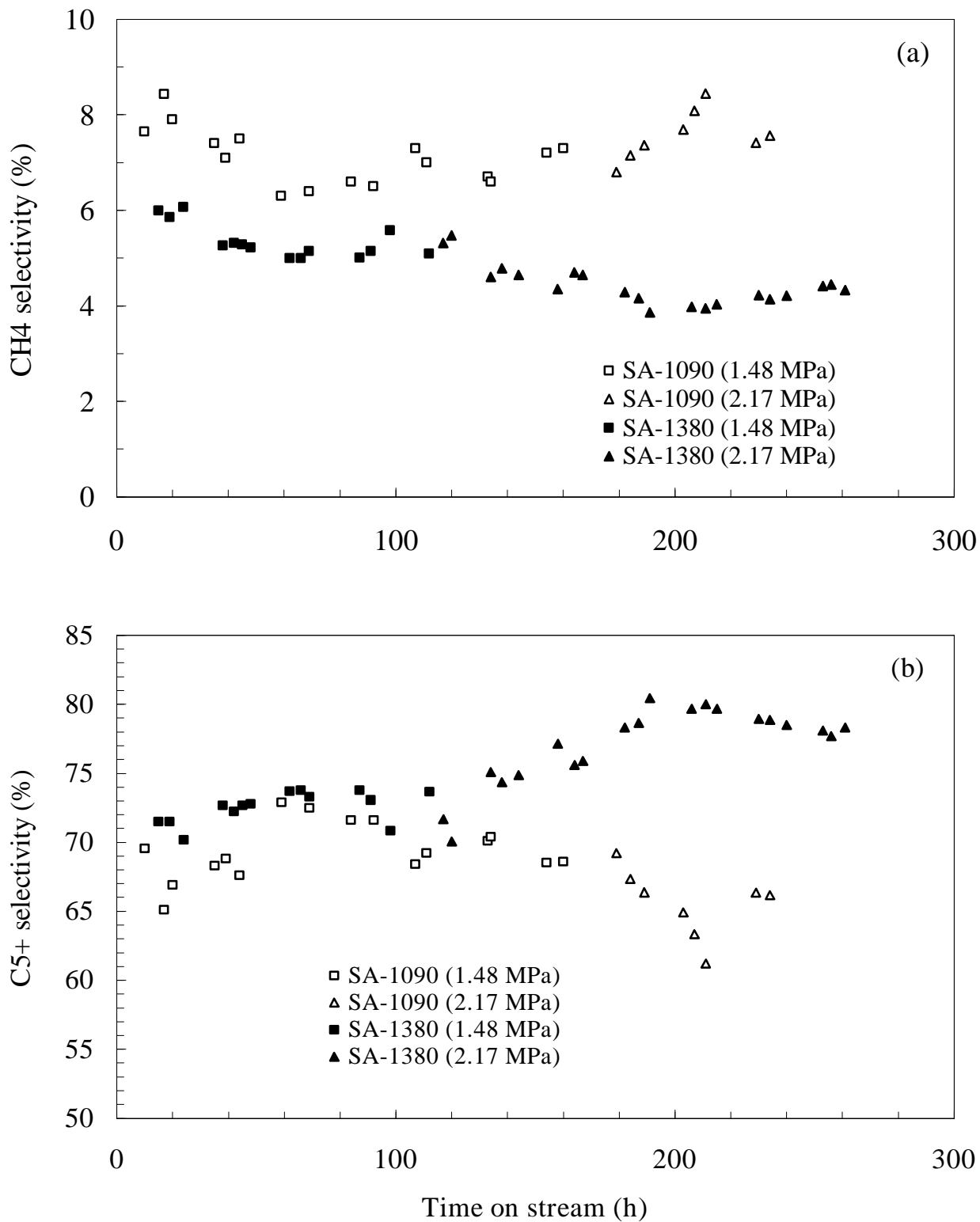


Figure 10 Effect of support type on hydrocarbon selectivity  
 (SA-1380 HP 14-150 Al<sub>2</sub>O<sub>3</sub> (calcined); SA-1090 Davison 948 SiO<sub>2</sub>)  
 Process conditions: 1.48 MPa & 4.0 NI/g-Fe/h; or 2.17 MPa & 5.9 NI/g-Fe/h

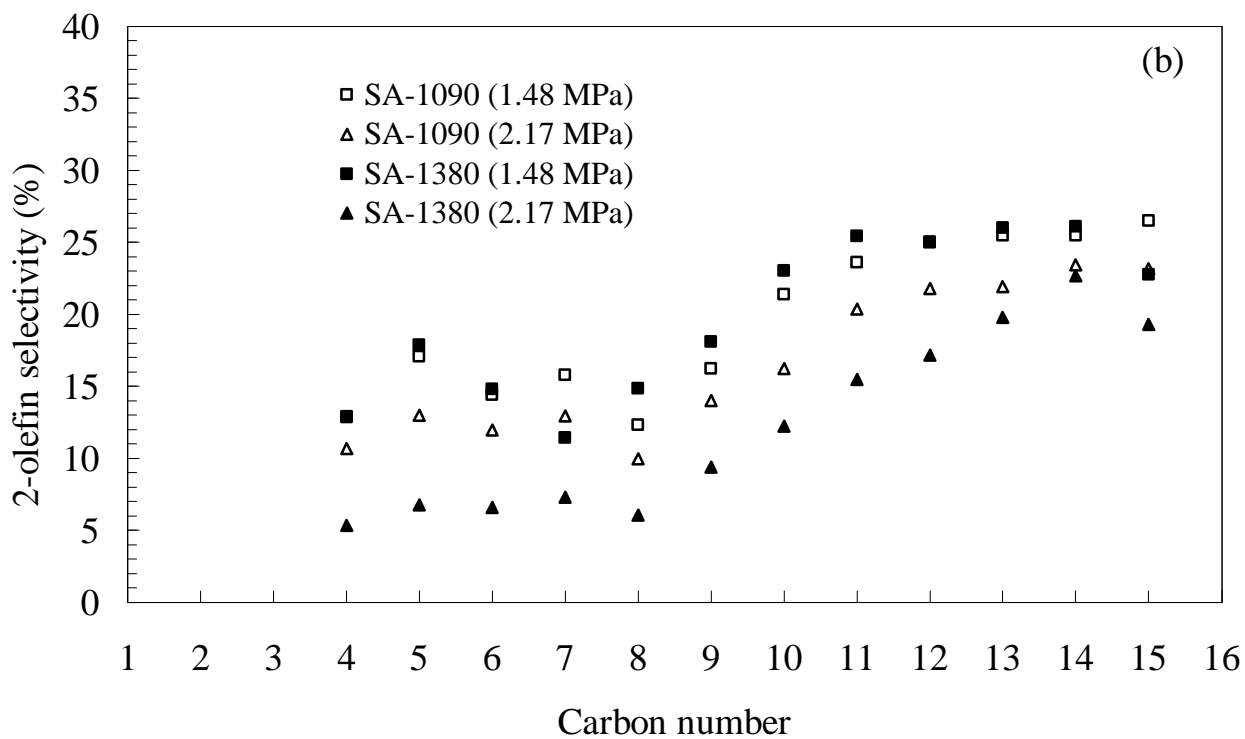
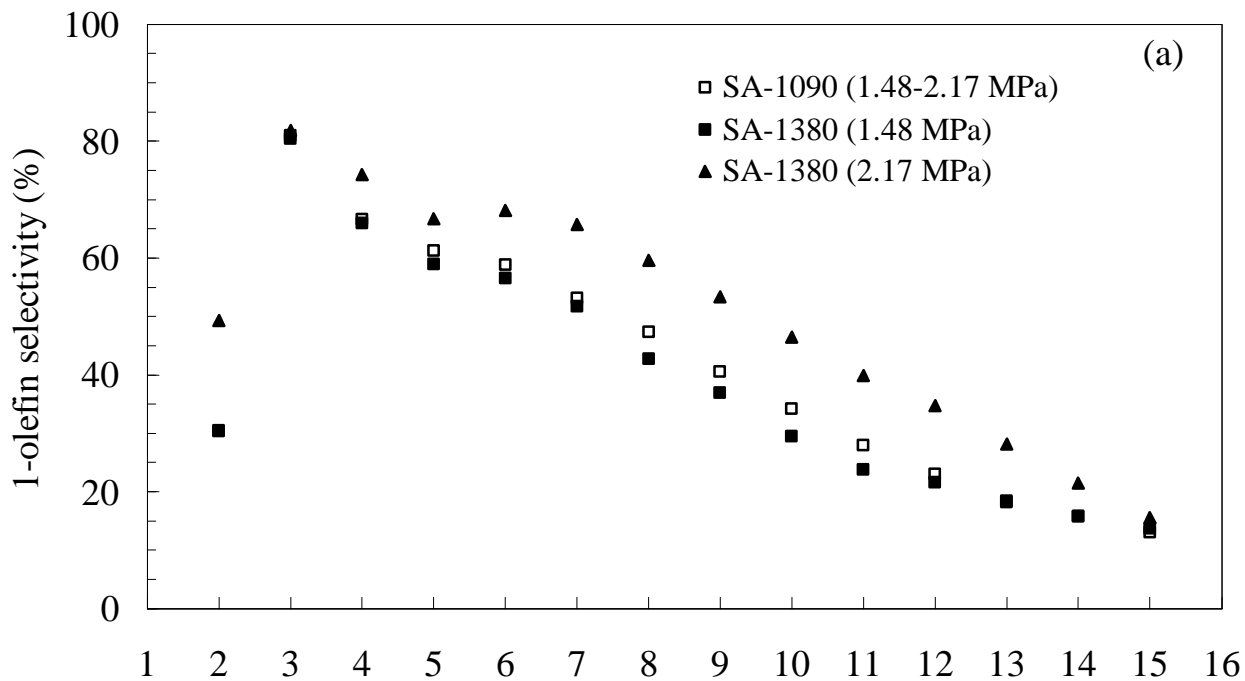


Figure 11 Effect of support type on olefin selectivity  
 (SA-1380 HP 14-150 Al<sub>2</sub>O<sub>3</sub> (calcined); SA-1090 Davison 948 SiO<sub>2</sub>)  
 Process conditions: 1.48 MPa & 4.0 NI/g-Fe/h; or 2.17 MPa & 5.9 NI/g-Fe/h

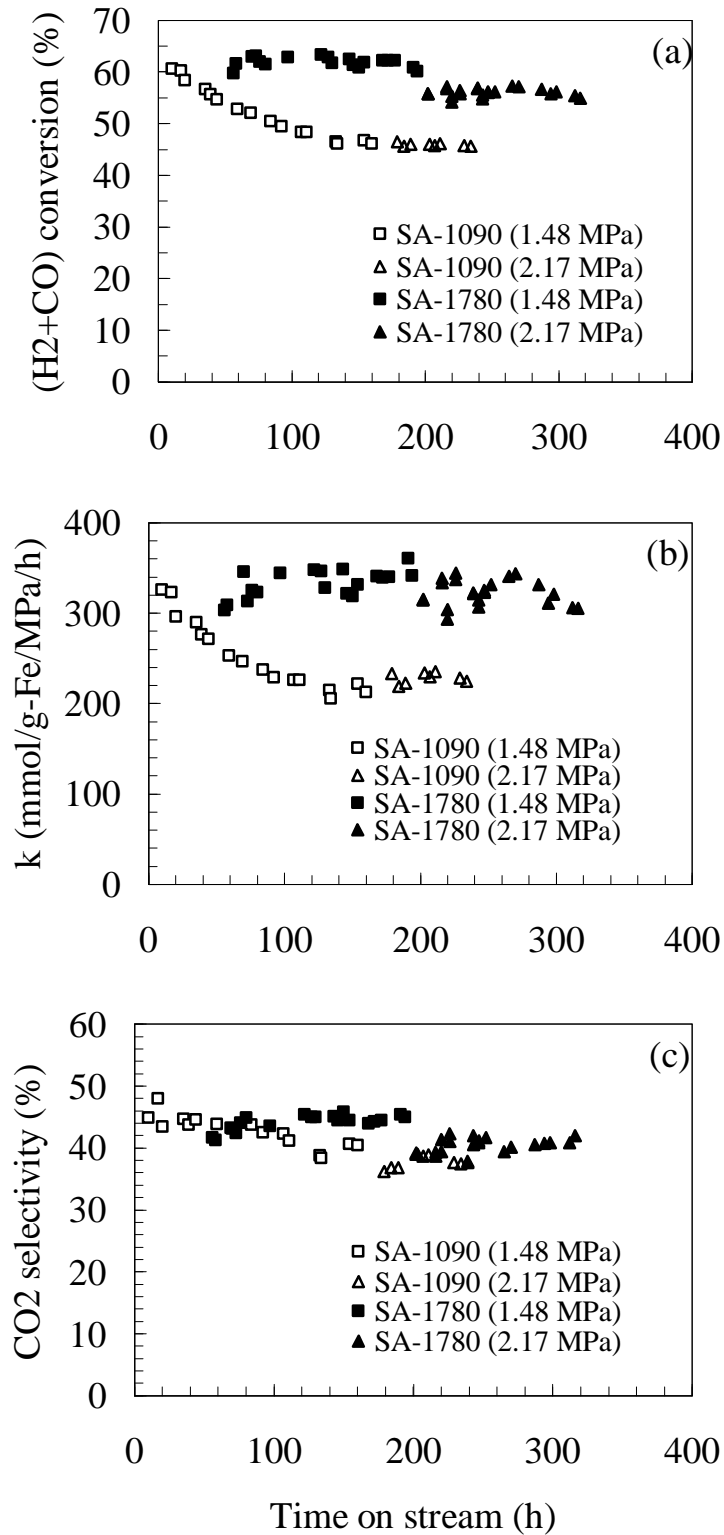


Figure 12 Effect of preparation procedure on F-T and WGS activity (SA-1090 aqueous solution; SA-1780 methanol solution)  
 Process conditions: 1.48 MPa & 4.0 NI/g-Fe/h; or 2.17 MPa & 5.9 NI/g-Fe/h

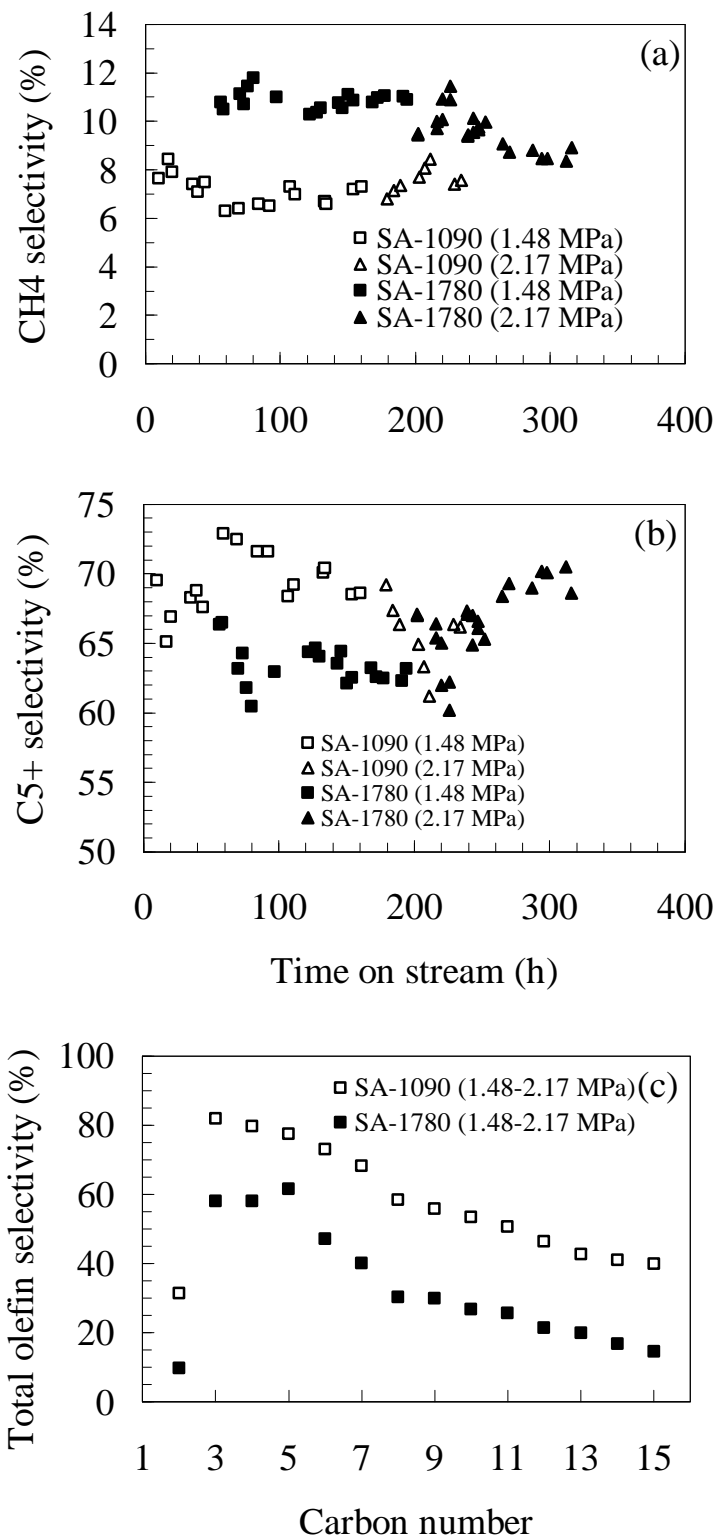


Figure 13 Effect of preparation procedure on product selectivity (SA-1090 aqueous solution; SA-1780 methanol solution)  
 Process conditions: 1.48 MPa & 4.0 NI/g-Fe/h; or 2.17 MPa & 5.9 NI/g-Fe/h

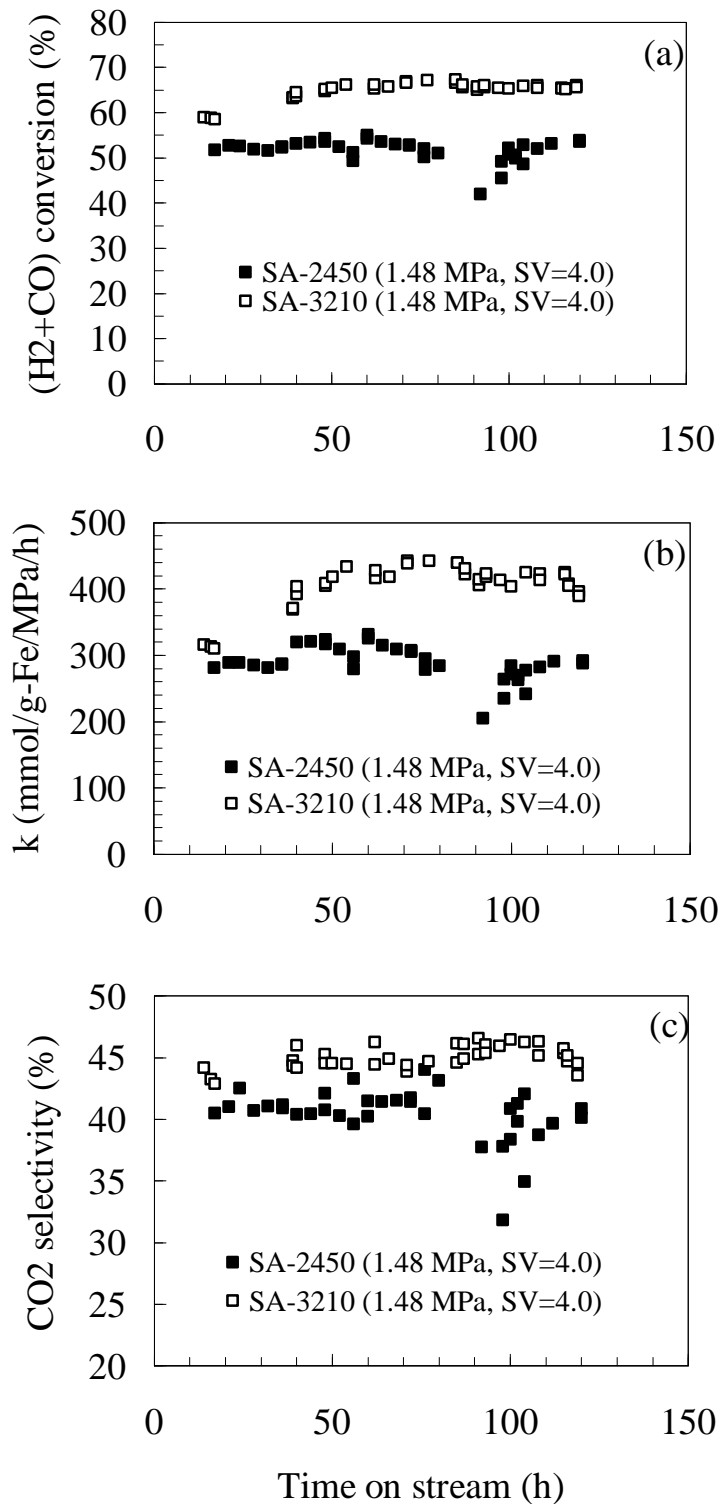


Figure 14 Effect of preparation procedure on F-T and WGS activity - Unpromoted catalyst (SA-2450 aqueous solution; SA-3210 methanol solution) Process conditions: 260°C, 1.48 MPa, 4.0 NL/g-Fe/h, H<sub>2</sub>/CO = 2/3

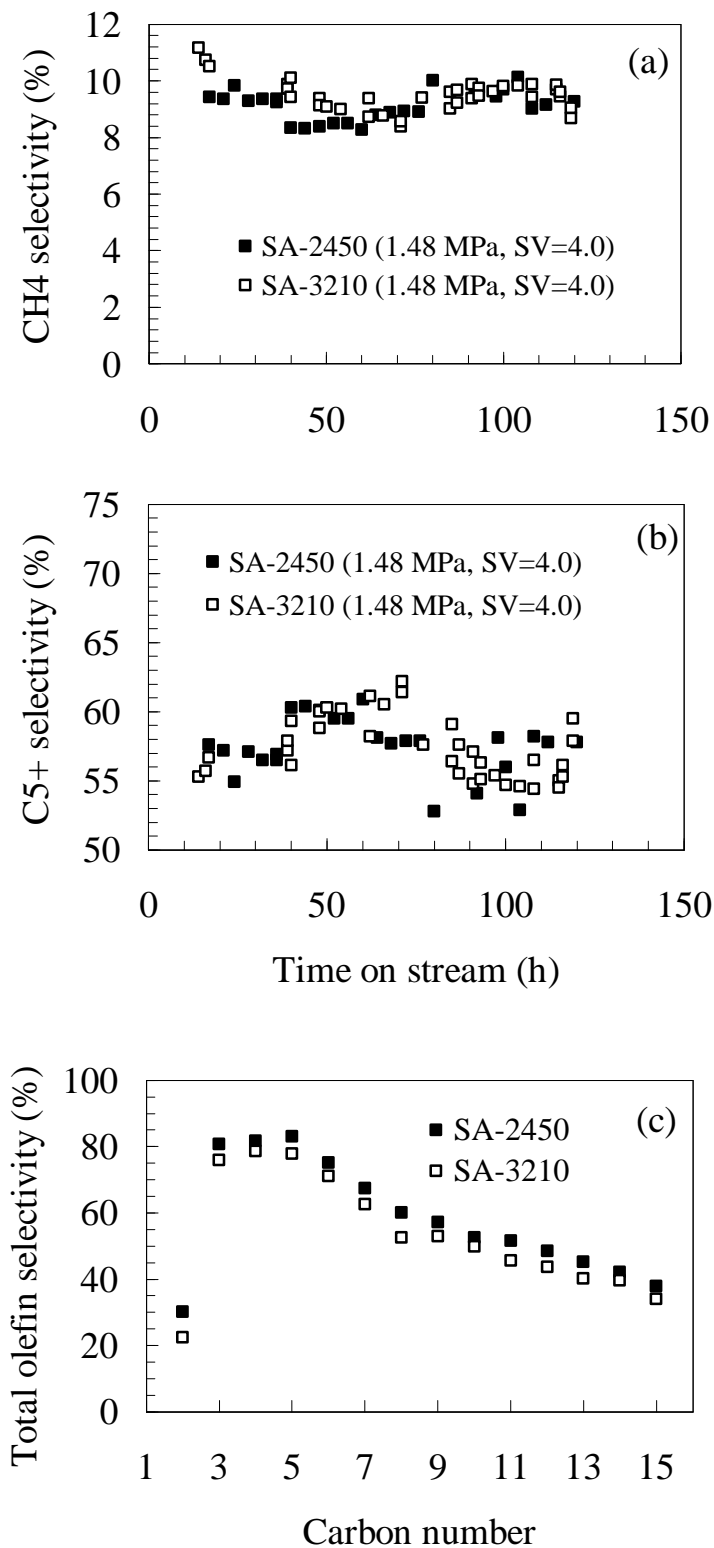


Figure 15 Effect of preparation procedure on product selectivity - Unpromoted catalyst (SA-2450 aqueous solution; SA-3210 methanol solution) Process conditions: 260°C, 1.48 MPa, 4.0 NL/g-Fe/h, H<sub>2</sub>/CO = 2/3



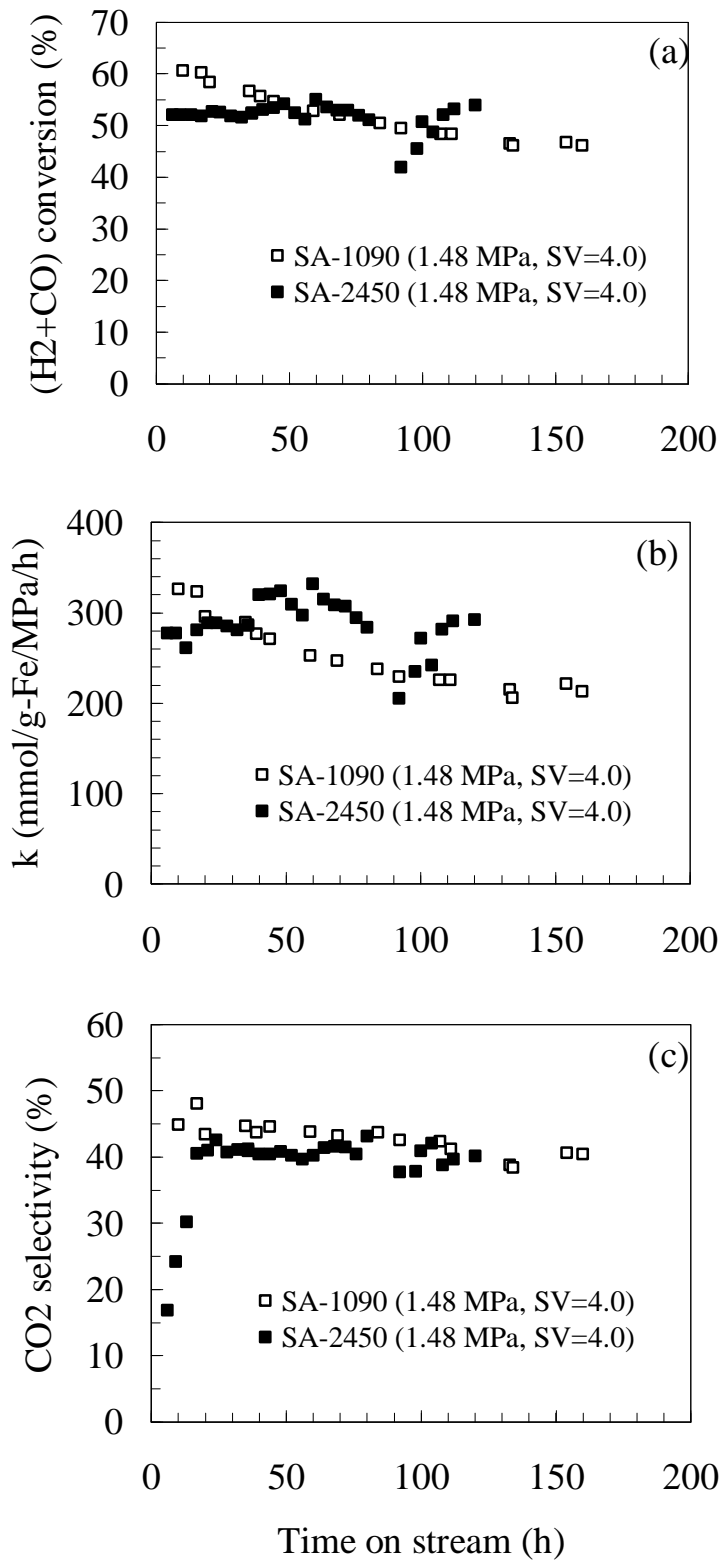


Figure 16 Promoter effects on the silica supported catalyst (aqueous impregnation) - F-T and WGS activity (SA-1090 promoted catalyst; SA-2450 unpromoted) Process conditions: 260°C, 1.48 MPa, 4.0 NI/g-Fe/h, H<sub>2</sub>/CO = 2/3

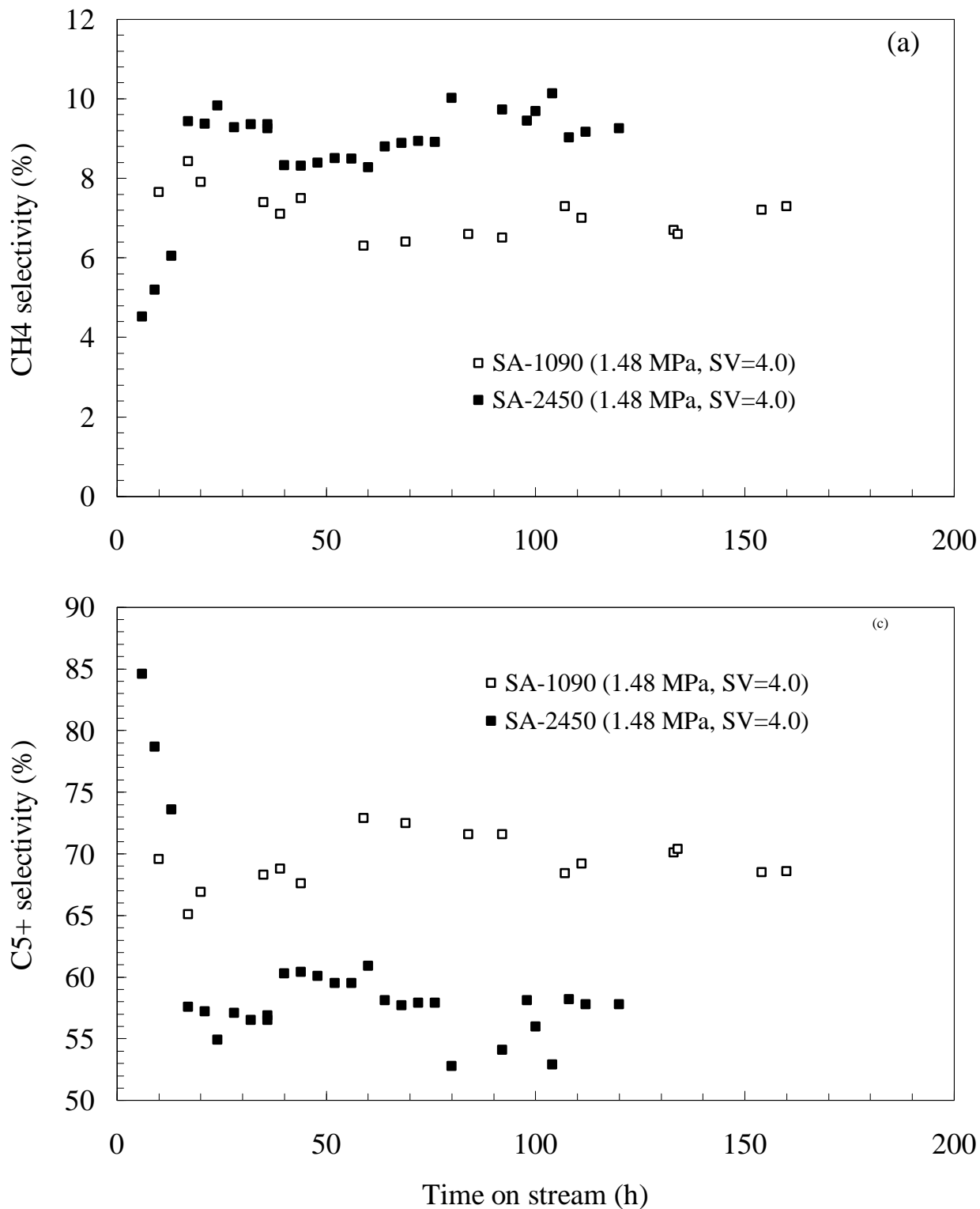


Figure 17 Promoter effects on the silica supported catalyst (aqueous impregnation) - Product selectivity (SA-1090 promoted catalyst; SA-2450 unpromoted) Process conditions: 260°C, 1.48 MPa, 4.0 NL/g-Fe/h, H<sub>2</sub>/CO = 2/3

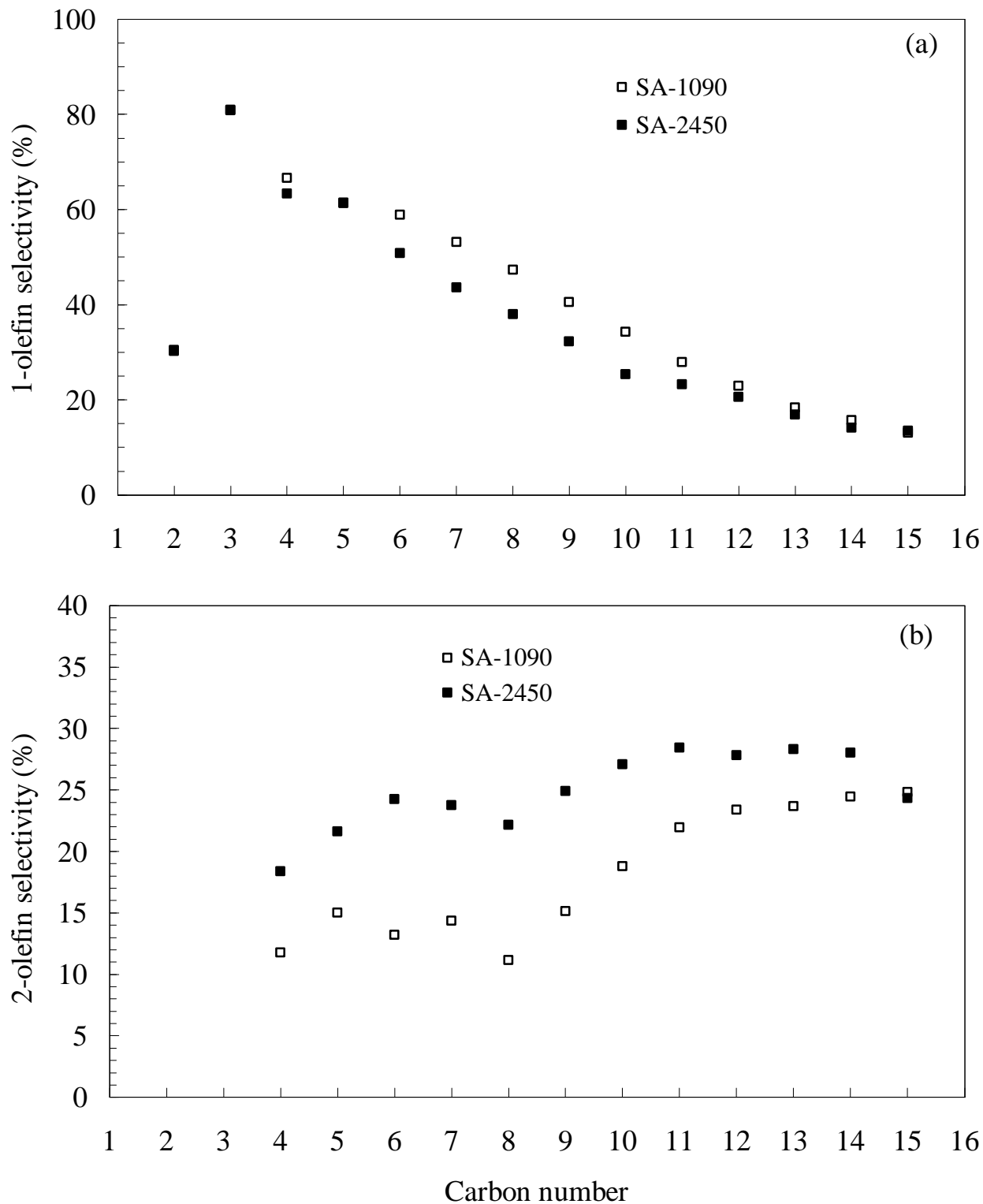


Figure 18 Promoter effects on the silica supported catalyst (aqueous impregnation) - Olefin selectivity (SA-1090 promoted catalyst; SA-2450 unpromoted) Process conditions: 260°C, 1.48 MPa, 4.0 NI/g-Fe/h, H<sub>2</sub>/CO = 2/3

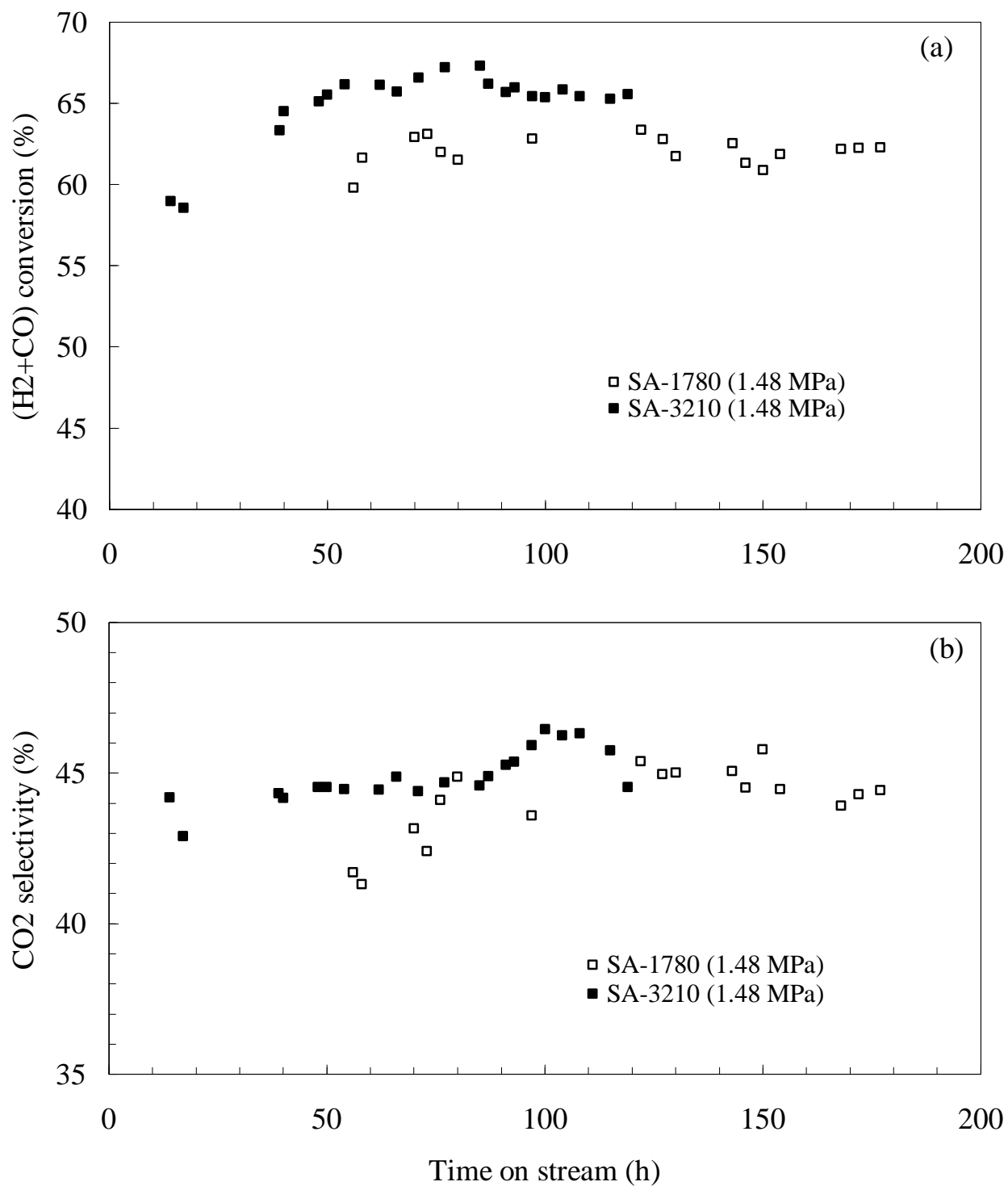


Figure 19 Promoter effects on the silica supported catalyst (organic impregnation) - F-T and WGS activity (SA-1780 promoted catalyst; SA-3210 unpromoted)  
 Process conditions: 260°C, 1.48 MPa, 4.0 NI/g-Fe/h, H<sub>2</sub>/CO = 2/3

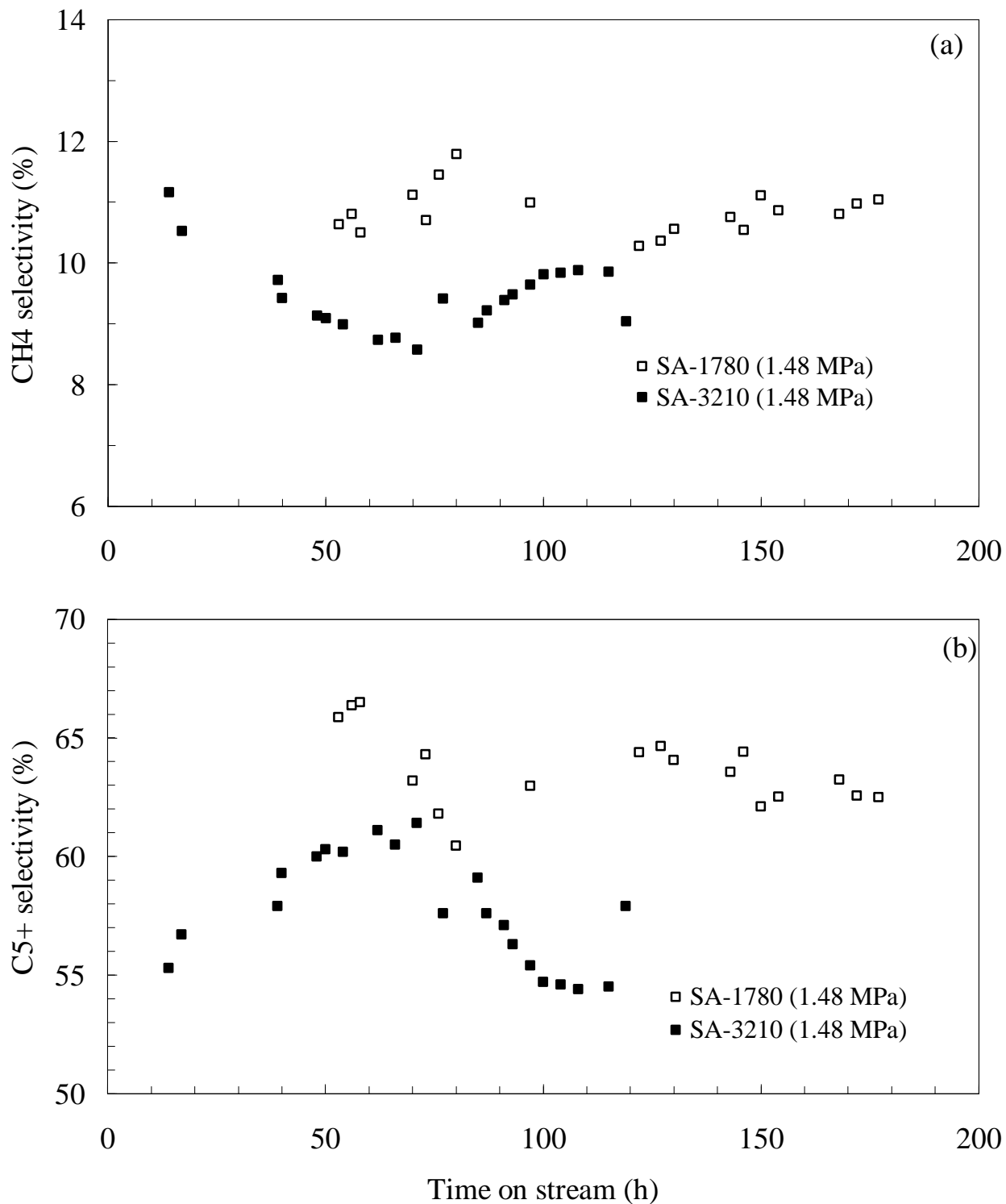


Figure 20 Promoter effects on the silica supported catalyst (organic impregnation) - Product selectivity (SA-1780 promoted catalyst; SA-3210 unpromoted) Process conditions: 260°C, 1.48 MPa, 4.0 NI/g-Fe/h, H<sub>2</sub>/CO = 2/3

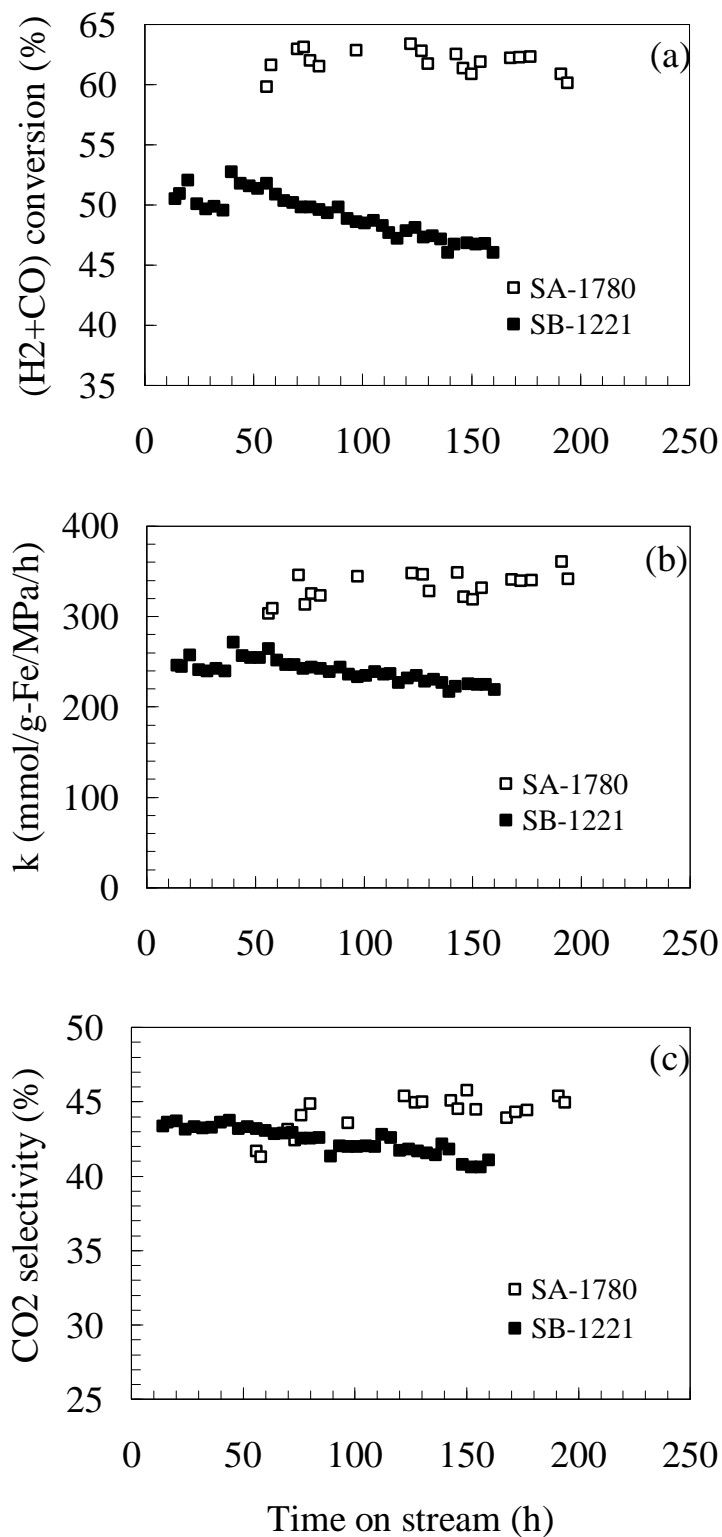


Figure 21 Effect of alkali promoter (silica supported catalyst - methanol solution) on F-T and WGS activity (SA-1780 K promoted; SA-1221 Na promoted) Process conditions: 260°C, 1.48 MPa, 4.0 NI/g-Fe/h, H<sub>2</sub>/CO = 2/3

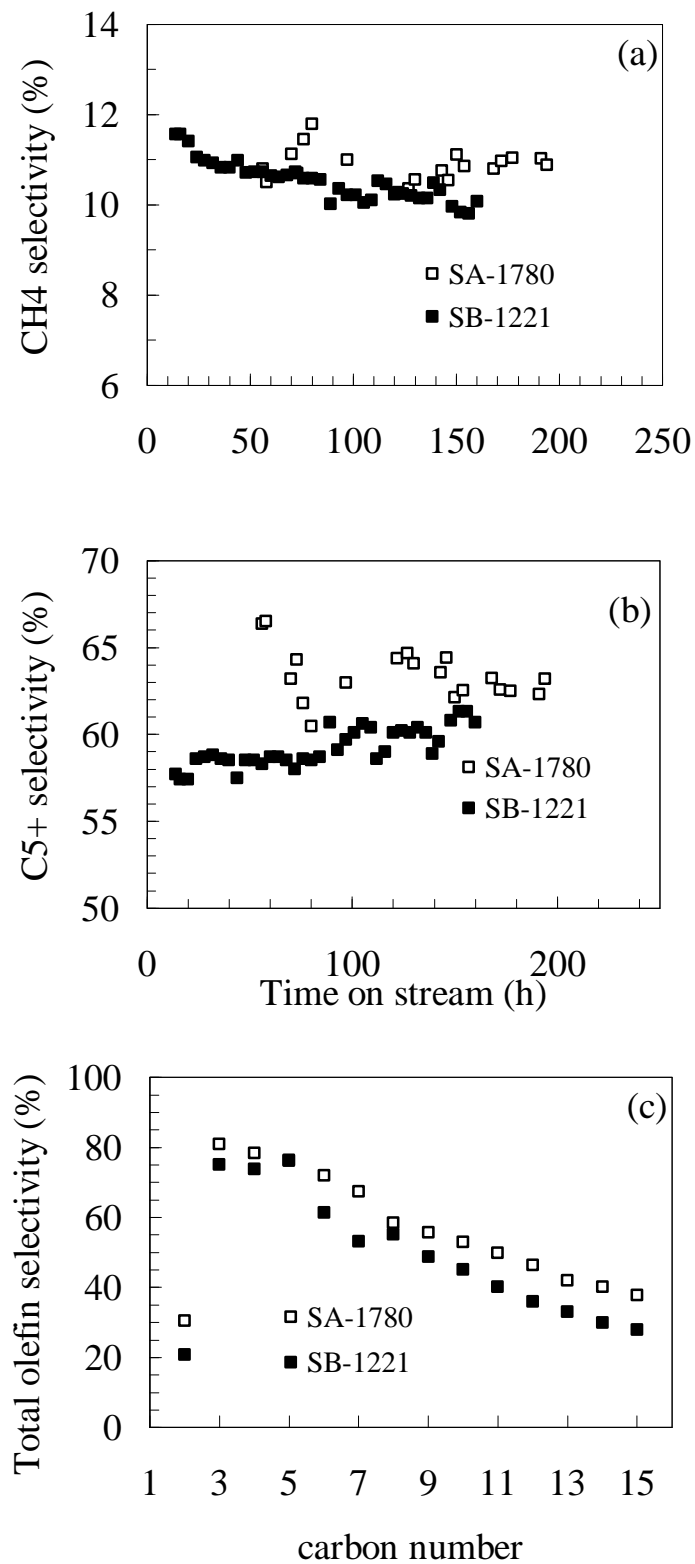


Figure 22 Effect of alkali promoter (silica supported catalyst - methanol solution) on product selectivity (SA-1780 K promoted; SA-1221 Na promoted) Process conditions: 260°C, 1.48 MPa, 4.0 NL/g-Fe/h, H<sub>2</sub>/CO = 2/3