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FLUIDIZABLE CATALYSTS FOR PRODUCING HYDROGEN BY STEAM REFORMING BIOMASS PYROLYSIS LIQUIDS

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INTRODUCTION

Initial work established that biomass pyrolysis oil could be steam-reformed to generate hydrogen using non-fluidizable (fixed-bed) commercial catalysts.[1] These multicomponent catalysts, which generally contain Ni, K, Ca, and Mg on alumina-based supports, are multifunctional and perform reforming, water gas shift, and gasification reactions. Our fixed-bed experiments showed that the carbohydrate-derived fraction of poplar pyrolysis oil could be almost stoichiometrically converted to hydrogen. However, process performance decreased with time because of char and coke deposition on the catalyst surface and in the bed itself thus limiting the reforming cycle to two or three hours. This cycle was even shorter when whole bio-oil or polymeric biomass-derived liquids (hemicellulose-rich fraction from biomass steam fractionation process) were used as feedstocks for hydrogen production.

Process performance was significantly improved by using a fluidized catalyst bed for reforming whole bio-oil and its fractions.[2] The fluidized bed configuration, which provides better contact between the reactants and the catalyst, significantly extended time-on-stream. Reforming experiments conducted in the fluidized bed system with the carbohydrate-derived fraction of pyrolysis oils have shown promising results. The fluidized catalyst exhibits a slow decrease in activity with time, which we have shown can be reversed by catalyst regeneration, either on- or off-stream. At the beginning of this project, we made a fluidizable catalyst material by grinding the pelletized commercial catalysts followed by screening out the desired particle size fraction. These particles show good catalytic activity but poor physical strength, as these materials were not designed for fluidized applications. The high attrition rate of the particles from fluidization results in excessive losses of catalyst solids from the reactor. Such losses are not economically viable for a potential industrial process.

The mechanical strength of the fluidized catalyst is a significant process issue that must be solved. To address this operational problem, we used a two-step approach to 1) identify and develop economical and attrition resistant support materials that could withstand high-temperature fluidization, and 2) prepare reforming catalysts from the best supports. The catalysts, containing NiO, MgO and/or K_2O, were then evaluated for attrition resistance and activity in a fluid bed system. We report here the results of support identification and catalyst performance evaluation.

EXPERIMENTAL

Support Identification

We pursued several routes to finding a fluidizable catalyst support that could withstand reforming conditions for extended operation. Sud-Chemie manufactured the fixed-bed catalyst from which the ground and sieved catalyst was made. This material consisted of Ni, Mg, and K supported on a mixture of alumina, silica, Portland cement and kaolin clay. Because we had unimpregnated support material in addition to catalyst from Sud-Chemie, the simplest approach was to determine if the support, developed for fixed-bed use, could be improved for fluidization use. A company with expertise in powder agglomeration and compaction looked at improving support mechanical strength through grinding, the addition of various binders, and subsequent compaction of the resultant materials. Such processing did not improve the mechanical strength of the Sud-Chemie support material. We then looked for other commercially available materials of reasonable cost that could have the required mechanical strength for fluidization. We began by searching for alumina-based materials as that is the primary support material for most reforming catalysts. We found that materials used as proppants in oil drilling and grinding media (manufactured by CarboCeramics) had the required mechanical strength though surface areas generally were too low ($< 0.05\ m^2/g$) to provide a reasonable catalyst support. We identified an alumina manufacturer (Coorstek Ceramics) that had readily available materials with the required properties. They were also able to tailor the properties of these aluminas to our requirements for particle size, surface area, and attrition resistance with existing processes and equipment.

Support Evaluation

The supports were evaluated for attrition resistance in a 2" fluidized bed reactor (Figure 1) for 48 hours. Simulated reforming conditions were: 850ºC, 2.5g/min fluidizing steam and 2.5g/min liquid water injected into the 250g-support bed with nitrogen. We used water as a surrogate for the pyrolysis oil feedstock to thermally stress the particles similar to the stress encountered during actual reforming. Support materials were characterized for surface area and particle size distribution before and after attrition tests. Weight losses of these materials were measured after exposure to these conditions and reported as % loss per day.

Catalyst Preparation and Evaluation

The best of the initial support materials, alpha alumina particles of 90-99% purity, were used to prepare several simple Ni-based catalysts to evaluate reforming activity, first with methanol and then with aqueous pyrolysis oil extract in a fluidized bed reactor. These catalyst compositions were modeled on commercial catalysts developed for reforming moderately heavy petroleum fractions. The catalysts contained from 0.08-3.3 wt% MgO, 0.25-8.3 wt% NiO and 0.05-1.0 wt% K_2O. Precursor salts included 99% $Ni(NO_3)_2 \circ 6H_20$ and $Mg(NO_3)_2 \circ 6H_2O$ (Alfa Aesar) and 99% KNO_3 (Aldrich). In general, Mg is used to stabilize Ni crystallite size and K to reduce coke deposition on the catalyst surface. All catalysts were prepared by addition of aqueous solutions of Ni, Mg, and K nitrate salts to the alumina supports to incipient wetness. The catalysts were calcined at 650ºC in air to convert the metal salts to oxides. The goal of the preliminary tests was evaluating catalyst activity and determining attrition losses from use during reforming. Running catalysts made from the supports under actual reforming conditions is the final step in evaluating attrition resistance as the addition of catalyst components could change support properties. The steam reforming experiments were also carried out using the bench-scale fluidized bed reactor system. Actual reforming conditions were similar with 2.5 g/min of either methanol or aqueous extracted pyrolysis oil replacing water from the attrition tests.

Fluidized Bed Reforming Reactor

The fluidized bed reforming system consisted of a tubular two-inch-diameter Inconel reactor that contained a perforated gas distribution plate and was externally heated by a three-zone electric furnace. The reactor could hold 250g of either support or catalyst. Before reforming, support or catalyst in the reactor was activated in a H_2/N_2 stream at temperature for 2 hours to reduce all metal oxide additives or to expose the supports to reaction conditions. The reactor solids were then fluidized using superheated steam generated in a boiler and heated to 750˚C before entering the reactor. Aqueous-extracts of pyrolysis oil were fed using a diaphragm pump. A specially designed injection nozzle, jacketed to provide temperature control of the feed entering the reactor, was used to spray liquids into the catalyst bed. The product collection line included a cyclone and a hot-gas filter to capture fine catalyst particles and char generated in the reactor. It also contained two heat exchangers to condense excess steam, which was collected in a vessel whose weight was continuously monitored. The outlet gas flow rate was measured by a mass flow meter and by a dry test meter. In reforming mode, the concentrations of CO_2, CO, and CH_4 in the reforming gas were continuously monitored by a non-dispersive infrared analyzer (NDIR Model 300 from California Analytical Instruments) and hydrogen by a thermal conductivity monitor (TCM4 from Gerhard Wagner, Germany). In addition, the gas was analyzed every 5 minutes by an on-line MTI gas chromatograph for hydrogen, carbon monoxide, carbon dioxide, methane, ethylene, and nitrogen content as a function of time. System temperatures and gas flows were recorded and controlled by an OPTO data acquisition and control system. Total and elemental balances were calculated as well as the yield of hydrogen generated from the feed. In all runs, catalyst remaining in the reactor, cyclone, and filter was recovered and weighed to measure attrition loss from the reactor.

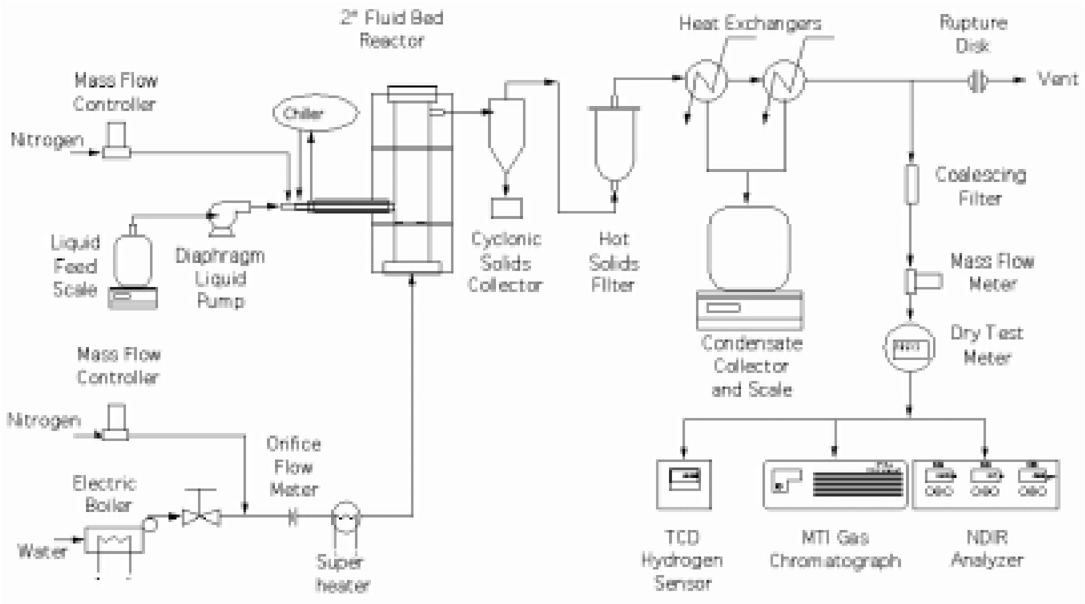

Figure 1: Schematic of the 2” fluidized bed reactor system

RESULTS AND DISCUSSION

Support Attrition Tests

Results of the support attrition resistance tests and the original commercial catalyst evaluation tests are summarized in Table 1. Both commercial catalysts were used for 48 hours of pyrolysis oil reforming and losses ranged from 28-33% of the original catalyst charge. The corundum material and most of the alumina samples exhibited acceptable attrition resistance after 48 hours of simulated reforming. Alumina samples 6 and 7 (90 and 99% alumina) had the best combination of attrition resistance and surface area. Sieve analysis, performed before and after attrition tests for all materials, showed loss of material from the reactor (as recovered in the cyclone) and any changes in particle size distribution. A representative sieve analysis (Figure 2) of the Al-6 material shows that none of the catalyst came out of the reactor during 48 hours of simulated reforming and that a small shift to smaller particle sizes occurred. The largest particle size shift was to the average particle size of the 90% Al_2O_3 material as received: screen number 45 (350-nm). Because the 90%Al_2O_3 preformed so well, we made a simple Ni-Mg catalyst from this material and ran it for 48 hours of methanol reforming to determine if catalyst addition and preparation changed attrition behavior. Sieve analysis showed a loss of 0.5 wt%/day from the reactor, the same loss as the support alone. This same catalyst was then used for reforming pyrolysis oil for 48 hours. Attrition losses were similar to the methanol experiment (<0.5% per day).[4] This result is key because it shows that catalyst preparation does not change support attrition resistance and that the catalyst is re-useable.

Table 1: Results of attrition tests for supports and catalyst/support materials after reaction. Wt % loss is the amount of catalyst entrained from the reactor (recovered in the cyclone) after testing or reaction divided by the amount of catalyst originally put into the reactor x 100.

Catalyst	Wt. in Reactor (g)	Wt. out Reactor (g)	% Loss	Surface Area (m^2/g)
Industrial Catalysts				
Commercial Ni Cat. 1 (Sud Chemie C 11 NK)	292.7	208.7	28.7	8.8
Commercial Ni Cat. 2 (ICI 46-1 S)	250.2	167.1	33.2	n/a
Industrial Supports				
Corundum (CarboCeramics)	250.0	249.9	0.4	0.03
Alumina-1	250.3	248.9	0.6	0.02
Alumina-2	250.1	219.5	12.2	0.07
Alumina-3	250.0	248.5	0.6	0.27
Alumina-4	92.5	89.5	3.0	2.7
Alumina-5	117.6	64.7	45.0	4.9
Auminal-6	251.4	248.8	1.0	0.2
Alumina 7	298.9	299.6	-0.2	1.4
Catalysts/Supports				
Ni-Mg/Alumina 6[1]	250.1	250.1	0.0	0.3

[1] with Ni after 48 hrs of methanol reforming

Based on the attrition test results, we chose the Coorstek alumina 6 and 7 supports to work with as they have required attrition resistance, reasonable surface area, and consist of alpha alumina, the desired support for reforming because of surface acid sites, which contribute to hydrocarbon cracking. They also were readily available in the kg amounts required for testing. Alumina 6 (90% alumina) as received contains 2% MgO and 1% CaO, which are reforming promoters. This material has a surface area limit of about 0.3 m^2/g but we can tailor promoter concentrations, with a concurrent surface area increase, during support manufacture at CoorsTek. Figure 3 shows scanning electron micrographs, taken at the same magnification (5000x), of the alumina 6 and 7 supports. The 90% alumina material (Al-6, surface area 0.2 m^2/g) has about seven times less surface area than the 99% alumina (Al-7, 1.4 m^2/g) and this difference is visible in the micrographs.

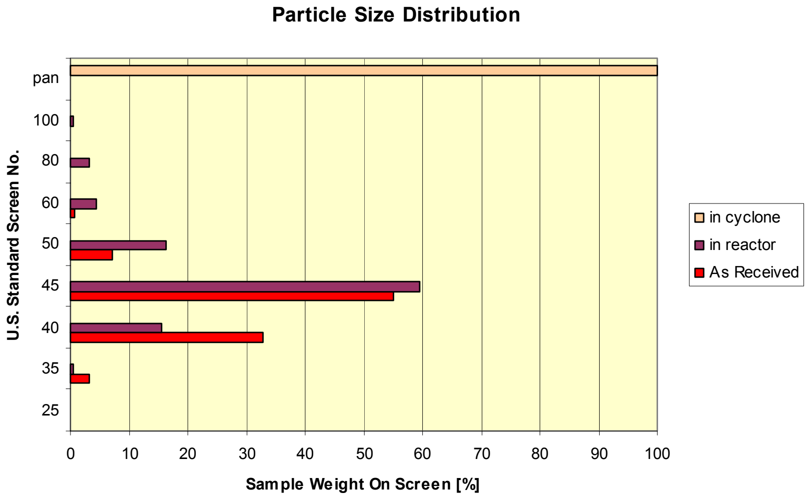

Figure 2: Wt % loss from the reactor and particle size distribution of alumina-6 (90% Al_2O_3) before and after attrition testing.

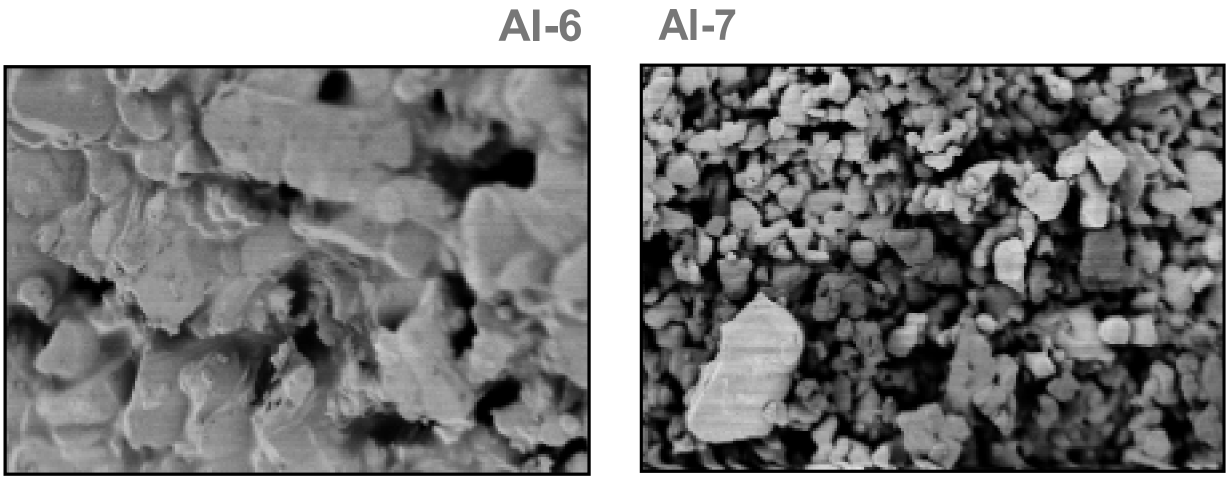

Figure 3: Scanning electron micrographs of the Al-6 and 7 supports taken at a magnification of 5000X. The surface areas are 0.2 and 1.4 m^2/g for Al-6 and Al-7, respectively.

Catalyst Composition

Composition data for all of the reforming catalysts based on the CoorsTek aluminas (supports 6-7, 90 and 99% Al_2O_3) are shown in Table 2a. Table 2b describes each preparation in detail.

All catalyst components were added as metal salt solutions to dry support in a rotating, angled drum reactor fitted with paddle blades that provided tumbling of the solids. For catalysts 1 and 2, a solution of Mg nitrate was added via pipette until incipient wetness of the support was reached. The wet solid was then transferred to ceramic trays and calcined in air at 650 °C for 4 hours. A sequential addition of Ni nitrate hexahydrate solution was then added to the Mg-containing support to incipient wetness and recalcined using the same conditions. Catalyst 2 went through this process three times for Mg addition and two times for sequential Ni addition. Catalyst 3, which only contained Ni, had the Ni salt solution added to hot support (60 °C) to maximize the amount of Ni that could be coated onto the support. Catalyst 4 was impregnated with a salt solution that contained all three components (Ni, K, Mg) followed by calcining and catalyst 5 was a repeat of the catalyst 4 preparation to verify method reproducibility. Catalyst 6 used a sequential addition of the three components to verify that both methods produce the same catalyst activity. Catalysts 7-9 were made on the higher surface area 99% alumina support and varied the component recipe used in catalyst 4. Component salt solutions were added in one step for these preparations.

Table 2a: Catalyst compositions made from the Al-6-7 alumina supports.

Catalyst Sample #	**Catalyst Prep. #**	**Support**	**Surface Area (m^2/g)**	**NiO (wt%)**	**MgO (wt%)**	**K_2O (wt %)**
1	1[a]	Al-6, 90% Al_2O_3	0.2	2.7	1.2	
2	2[b]	Al-7, 99% Al_2O_3	1.0	4.1	3.3	
2a	2[c]	Al-7	1.0	4.1	3.3	
2b	2[d]	Al-7	1.0	4.1	3.3	1.0
3	3[e]	Al-6	0.2	8.3		
4	4[f]	Al-6	0.2	1.8	0.15	0.10
4a	4[g]	Al-6	0.2	1.8	0.15	0.10
5	5[h]	Al-6	0.2	1.8	0.15	0.10
6	6[i]	Al-6	0.2	1.8	0.15	0.10
7	7[j]	Al-7	1.0	1.8	0.15	0.10
8	8[k]	Al-7	1.0	1.8	0.6	0.50
9	9[l]	Al-7	1.0	0.25	0.08	0.05

Table 2b: Preparation method for each catalyst described in Table 2a.

Catalyst Prep. #	**Preparation Method**
1[a]	Incipient wetness method (IW), sequential MgO impregnation then NiO
2[b]	IW, sequential 3x impregnation MgO, 2x impregnation NiO
2[c]	Catalyst no. 2, re-calcined to regenerate after 2” reactor test
2[d]	Cat. 2 retested in 2”, recalcined, K added from KOH solution
3[e]	IW on hot support with hot $Ni(NO_3)_2$ solution
4[f]	IW, all-in-one (soup) addition of Ni, K, Mg as nitrate solutions
4[g]	Catalyst 4 regenerated via calcining after reaction
5[h]	Repeat preparation (soup) of catalyst 4
6[i]	Repeat cat 4 preparation with sequential K, Mg impregnation, calcining, then Ni
7[j]	Catalyst 4 preparation (soup) on 99% alumina support
8[k]	Repeat catalyst 7 preparation but increase K and Mg content
9[l]	IW, all-in-one addition of reduced Ni, K, Mg contents

To characterize fresh and used catalyst surfaces, we used scanning electron microscopy with a back scattering technique that images heavy molecular weight species on surfaces. Representative SEM’s (5000x magnification) of catalyst 7 before and after pyrolysis oil reforming are shown in Figure 4. The light colored areas seen in Figure 4a show the NiO deposits that form after calcining freshly prepared catalyst. The unused surface, reasonably uniform in appearance, changes after use (b): large filled-in areas appear, likely due to coke deposition, and the amount of NiO deposits is reduced. It is also likely that coke deposits cover up some of the active NiO deposits. After use, the catalyst surface has a dark gray color, characteristic of coke. Loss on ignition tests of the used materials show that the amount of coke on the surface is very low: < 0.1 g per catalyst charge of 250 g.

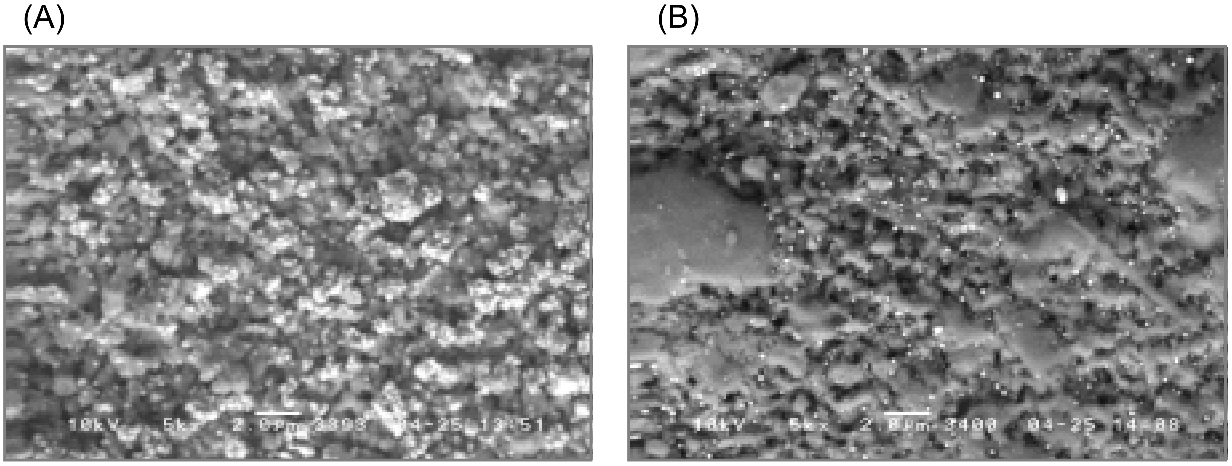

Figure 4: SEM micrographs (5000x magnification) of catalyst 7 (1.8 wt% NiO) before and after 8 hours of reforming pyrolysis oil. Micrograph A is unused catalyst and the light areas show NiO deposits. Micrograph B is used catalyst.

Catalyst Evaluation

All tests were conducted with the aqueous fraction of pyrolysis oils from pine softwoods. We used the CO_2/CO ratio to measure selectivity for water-gas shift and coke gasification and the H_2/CH_4 ratio to measure reforming selectivity. The selectivity ratios were calculated by averaging concentrations from the first 3 hours of reaction for all catalysts (Table 3a) and from 20-23 hours for those catalysts run for longer duration: the commercial catalyst C-11NK and NREL-prepared catalysts 1 and 5-9 (Table 3b). Overall activity is measured by the H_2 yield, which is the ratio of actual yield to theoretical yield x 100. Theoretical yield is the amount of hydrogen produced if reforming and water-gas shift reactions convert all carbon in the feedstock to CO_2.

Table 3a: Catalyst selectivity data for reforming aqueous pine pyrolysis oil calculated during the interval 0-3 hours of reaction.

Catalyst	**Wt % Ni**	**Wt % Mg**	**Wt % K**	**Support % AL_2O_3**	**CO_2/CO**	**H_2/CH_4**	**H_2 Yield**
C 11 NK	19.0	5.0	8.0	Mix	4.0	594	90
99% Al_2O_3				99	1.2	18.1	81
Cat 1	2.7	1.2		90	4.5	232	91
Cat 2	4.1	3.3		99	2.6	9.7	70
Cat 3	9.0			99	3.2	23.3	87
Cat 4	1.8	0.15	0.10	90	6.6	937	94
Cat 5	1.8	0.15	0.10	90	7.7	665	95
Cat 6	1.8	0.15	0.10	90	5.1	593	92
90% Al_2O_3				90	1.2	18.1	81
Cat 7	1.8	0.15	0.10	99	5.1	593	92
Cat 8	1.8	0.6	0.5	99	5.3	135	92
Cat 9	0.25	0.08	0.05	99	3.1	20.7	86

Table 3b: Catalyst selectivity data for reforming aqueous pine pyrolysis oil calculated during the interval 20-23 hours of reaction.

Catalyst	Wt % Ni	Wt % Mg	Wt % K	Support % AL_2O_3	CO_2/CO	H_2/CH_4	H_2 Yield
C 11 NK	19.0	5.0	8.0	MIX	4.1	39.6	91
Cat 1	2.7	1.2		90	0.7	27.5	70
Cat 6	1.8	0.15	0.1	90	4.4	28.5	91
Cat 7	1.8	0.15	0.1	99	4.4	28.4	91
Cat 8	1.8	0.6	0.5	99	4.8	22.9	91
Cat 9	0.25	0.08	0.05	99	3.1	20.7	86

The benchmark for this work was the performance of the commercial catalyst C-11 NK. We additionally ran the supports Al-6 and 7 with pyrolysis oil to determine the effect of thermal cracking on hydrogen production. We began with simple formulations of Ni and Mg to assess catalyst performance. Our first catalyst (Cat-1) contained 2.7% Ni and 1.2% Mg on 90% alumina with 0.2 m^2/g surface area. During the first three hours of use, this catalyst had shift/gasification activity comparable to the industrial catalyst but reforming ability was reduced. Performance during the 20-23 hour period showed that carbon-to-gas conversion and hydrogen yield were significantly reduced compared to the commercial material, though reforming activity stabilized. This result suggests that potassium is necessary to stabilize water-gas shift and coke gasification activity. The second catalyst, which contained more Ni and Mg than Cat 1, was made on the higher surface area Al-7. All performance measures were significantly reduced with this catalyst. The third material consisted of 8.3% Ni on Al-7 and both reforming and shift performance improved. Performance of this catalyst clearly demonstrates the effect of Ni on reaction rates.

Because the first three catalyst compositions did not meet the performance of the commercial material, we decided to scale the proportion of additives to the industrial catalyst composition, C 11 NK, based on available surface area of our supports. We were able to get more material than was proportionally required as we added the impregnating salt solution to incipient wetness. Preparations 4-5 are identical, use 90% alumina as the support, and were prepared with sequential impregnation and calcining steps. These catalysts (4-5), which were on stream for only 6 hours, show improved shift, gasification and reforming activity for the first 3 hours but activity slowly declined during the last 3 hours of use. Reproducibility was good for these two identical preparations and initial reforming and shift rates are better than the C-11 material. Catalyst 6 was prepared using an “all in one” addition of Ni, K, and Mg to the support. We wanted to determine if this simpler preparation would give similar performance to catalysts 4 and 5, which were made by sequential addition and calcination steps. Catalyst 6, during both short and long term use, had comparable shift/gasification and reforming activity as the commercial catalyst. Overall performance was similar to the sequentially prepared materials and all successive materials were prepared with the simpler “all in one” or “soup“ method. The 90% alumina experiment gave the same results as the 99% material. This result suggests that surface area does not appear to affect thermal cracking of the feedstock.

Catalysts 7-9 were made with Al-7 and the compositions explore the boundaries of the recipe used successfully in catalysts 4-6. Figure 4 plots H_2, CO, CO_2, and CH_4 concentration versus reaction time for catalysts 7-9 and C-11 NK. Note that these multicomponent catalysts are designed to perform the following reactions:

Reforming: CxHyOz + H_2O <----> H_2 + COx
Water Gas Shift: $H_2O + CO$ <----> $CO_2 + H_2$
Steam Gasification: $C + H_2O$ <----> $CO + H_2$

Catalyst 7 is identical in composition to catalysts 4-6 with the added components scaled to match the increased surface area. Short-term performance was slightly better overall than C-11 and the shift reaction showed a 20% improvement. Long-term performance remained similar to the commercial material though reforming activity was reduced. Interestingly, catalysts 6 and 7 behave identically though they are made with different supports. This result again suggests that surface area, at these low levels, does not significantly impact catalyst performance. Catalyst 8, which contains 4x more Mg and 5x more K than catalyst 7, exhibited a reduction in reforming activity for both short and long duration reaction though the shift performance remained unchanged. The Ni concentration was not changed in this material and it is possible that the additional K and Mg covered some of the Ni surface, which would account for reduced reforming ability. The last composition, catalyst 9, contained significantly reduced amounts of all components and it exhibited reduced performance for reforming, shift, and overall H_2 yield.

Figure 5 shows that our catalysts generally have better reforming rates than the commercial material as the H_2 yields are higher for catalysts 7 and 8. This result tracks Ni content as catalyst 8 likely has less NiO available for reaction (Ni covered by increased amounts of K and Mg oxides). Our materials, however, need improvement in the shift and steam gasification reactions, as CO_2 gas concentrations are lower for catalysts 7-8 compared to C-11. Interestingly, catalyst 9 forms CO as well as the commercial material though CO_2 production remains similar to catalysts 7-8. Methane production is increased in all of our catalysts and the least amount forms with catalyst 7. Note that Ni/Al_2O_3 also functions as a methanation catalyst.

These results indicate that we have established the boundary compositions for the three-component, multifunctional catalyst for producing hydrogen from pyrolysis oil reforming. The supports have the required mechanical strength for fluidization and catalyst 7 yields the best overall performance for H_2 production. We will next focus on optimizing composition to increase shift activity and suppress methanation. We will use a multivariate approach to begin to understand how catalyst composition affects reforming chemistry within this data set. We additionally intend to test other support materials (when available) and add other reforming promoters and catalysts (Ca, Fe, La). [5]

SUMMARY AND CONCLUSIONS

Most of the alumina materials tested exhibited improved attrition resistance under steam reforming conditions compared to that of commercial fluidized reforming catalysts though surface areas are about an order of magnitude less. The best support materials were CoorsTek 90 and 99% alumina particles with surface areas of 0.2-1.4 m^2/g. Attrition losses for these materials were less than 0.5 wt% per day. Catalysts made from the CoorsTek supports and containing Ni, Mg, and K oxides exhibit increased shift/gasification activity and significantly improved reforming ability compared to the industrial material for the first 3 hours of reaction. From 20-23 hours, we observed a reduction in shift/gasification activity for both the NREL and commercial catalysts. Catalyst 7 had comparable performance to the commercial catalyst during 24 hours on stream: both shift and gasification activity were slightly better and reforming activity moderately reduced compared to the commercial material, which has an order of magnitude more surface area. While we have a support/catalyst system that works about as well as the commercial catalyst (C-11 NK), further optimization of support and catalyst composition may yield even more active and selective catalysts.

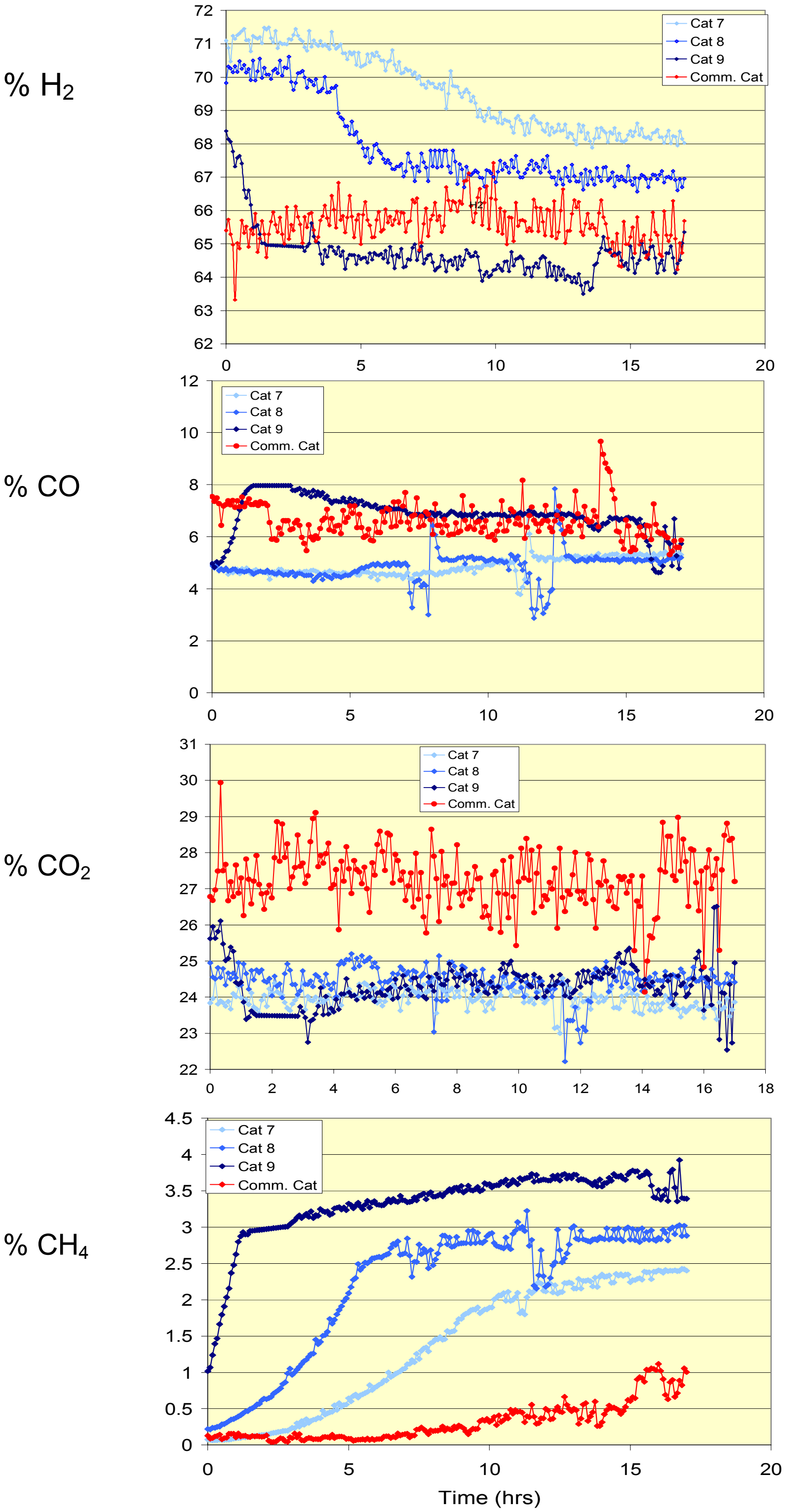

Figure 5: Reaction gas composition data versus reaction time for catalysts 7-9 and C-11 NK.

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