

Low Severity Coal Liquefaction Using Intermetallic  
Hydrides as Both Catalysts and Hydrogen Distribution Agents

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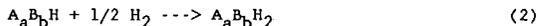
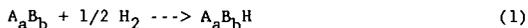
ABSTRACT

Several intermetallic alloys are capable of forming reversible hydrides by storing atomic hydrogen within their metal matrices at densities that may exceed that of liquid hydrogen. In this paper we examine FeTi, LaNi<sub>5</sub>, CaNi<sub>5</sub>, Mg<sub>2</sub>Cu, and Mg<sub>2</sub>Ni as materials to both transport and distribute hydrogen to slurried coal while catalyzing the liquefaction process. Liquefaction experiments were performed in 5 ml microreactors using Alabama Black Creek coal slurried in 1-methylnaphthalene at temperatures of 316, 371, and 427 °C and a pressure of 4.83 MPa. Catalyst activity followed the general trend of CaNi<sub>5</sub> = LaNi<sub>5</sub> > FeTi > Mg<sub>2</sub>Cu > Mg<sub>2</sub>Ni with total conversions of greater than 60% obtained from the first three catalysts. As the reaction temperature increased, the higher conversions favored the production of additional preasphaltenes and oils. The CaNi<sub>5</sub> catalyst proved to be the most selective towards oils. Noncatalyzed conversion results were approximately half that of the most active catalytic intermetallic hydrides at the temperatures investigated. The catalysts were recovered after a single wash with THF and with the exception of LaNi<sub>5</sub> showed no visual evidence of coking. Previous results have shown that FeTi catalyst was deactivated by 4% after liquefaction at 260 °C and 4.14 MPa. A possible explanation for the increased activity at reduced severity may be that hydrogen is supplied to the surface by the intermetallic hydride making the surface self-cleaning.

INTRODUCTION

Nickel molybdenum and cobalt molybdenum supported on alumina have been studied by many researchers as catalysts for direct coal liquefaction [1-3]. These bimetallic supported catalysts show increased activity, stability, and selectivity when compared with pure nickel and cobalt similarly supported on alumina, but deactivate rapidly under liquefaction conditions [4,5]. These surfaces may be and often are blocked by metal contaminants or organic layers which will not permit hydrogen chemisorption, thereby reducing the liquefaction rate compared to that of a fresh catalyst charge. What is needed is a self cleaning approach which continuously renews the surface while delivering atomic hydrogen to the catalytic sites.

Several intermetallic alloys are capable of forming reversible hydrides by storing atomic hydrogen within their metal matrices. This paper concentrates on FeTi, LaNi<sub>5</sub>, CaNi<sub>5</sub>, and Mg<sub>2</sub>Cu. When properly conditioned and exposed to hydrogen at room temperature, these alloys form reversible metal hydrides according to the following general reactions [6-9]



Depending upon the temperature and pressure, these intermetallic matrices are capable of reversibly storing hydrogen at densities exceeding that of liquid hydrogen. Since the absorption process is exothermic, a matrix which has been

fully hydrided at room temperature will desorb atomic hydrogen at the metal surface when subjected to reactor temperatures. A drop in pressure will also result in the release of hydrogen from the intermetallic hydride. Thus, these compounds will deliver atomic hydrogen to the catalytic surface when taken from ambient to reaction temperature.

Intermetallic compounds differ chemically from their pure components. For FeTi, the elements react with carbon, oxygen, and nitrogen forming extremely stable compounds. When alloyed, this intermetallic compound has the hydride properties previously described and is virtually immune to oxidation, nitration, and carbide formation under normal liquefaction reactor conditions. Furthermore, Fe<sub>x</sub>Ti alloys have been shown to have substantial catalytic activity towards hydrogenation reactions [10-13].

These compounds also serve as bimetallic catalysts, and their use in the bulk form eliminates the pore diffusion, pore blockage, and particle sintering problems encountered with supported metal catalysts. Supported metal catalysts deactivate by coking resulting in site blockage and metals deposition which causes pore mouth clogging. Stiegel and coworkers [4] found that the deactivation by metals deposition was primarily due to the oxides of Fe, Ti, Na, Ca, and Mg. Some of the intermetallic hydrides discussed here, may show some immunity to metals deposition because they contain one or more of these elements in their structure. Finally, it is theorized that desorbing hydrogen sweeps contaminants from the surface preventing their deposition.

In a previous study [14], FeTiH<sub>2</sub> was used to catalyze the liquefaction of Utah and Alabama coals in a 1-liter batch reactor. Conversions of approximately 50% were obtained in 30 minutes at 260°C and 4.14 MPa while suffering only a 4% catalyst deactivation. This research incorporates 5 ml microreactors to decrease the cost of materials, reduce analysis time for quicker catalyst screening, and to more accurately control the amount of catalyst and reaction times used. This approach permitted a more rapid extension of our initial FeTi investigations to include LaNi<sub>5</sub>, CaNi<sub>5</sub>, and Mg<sub>2</sub>Cu.

## EXPERIMENTAL

### EQUIPMENT

The microreactor system has many advantages over the 1-liter autoclave previously used [14]. The most important advantage is that the amount of catalyst in the sample is always known. In the 1-liter system, the catalyst was activated (hydrided) in a separate tubular reactor and then added to the coal slurry at reaction conditions. The catalyst swelled during hydrogen absorption causing catalyst packing in the hydride vessel, which made it difficult to deliver a uniform catalyst charge to the reactor. The microreactor system eliminated this problem by adding the coal slurry to the intermetallic hydride catalyst which was prepared in the microreactor.

The microreactor, discussed below, is a modified version of the tubing bomb technique used by Maa and coworkers [15]. The system consisted of two microreactor units, mounted on a shaker for agitation, that can be submerged in either a sand bath or a water quench tank. The sand bath and quench tank allowed for a much faster heat up and cool down period than the previously used 1-liter reactor system.

### Microreactor unit

A schematic drawing of a microreactor unit is shown in Figure 1. The unit was designed with two chambers to enable separate catalyst hydriding and coal slurry preparation to be performed. The coal slurry reservoir was manufactured by modifying a Kerotest Shutoff Valve (part # T-110N-35-004-A03). As originally provided, this valve had 1/2" NPT male X female connections. The threads were removed from both ends, with the male end being further machined to weld to a 1/2" deep 5/8" O.D. hole in the Y fitting. One end of a

1/2" O.D. 37° flared tube hex union was machined flush with the hex and welded to the female end of the slant valve. This design allowed the slurry reservoir to be accessed for coal and solvent addition as well as cleaning purposes, while maintaining the full internal volume of the female entrance to the valve. The line attached to the remaining end of the flared union provided sources of vacuum, venting, hydrogen, and helium by connecting to the 1-liter reactor system (see Figure 2). A slant valve was chosen to facilitate the addition of the coal slurry to the reaction vessel by making the pathway as vertical as possible. The hydride conditioning and liquefaction reaction vessel consisted of a 1/2" O.D. socket weld branch to 37° flared tube tee. The removable caps allow for catalyst addition prior to the run and product recovery and reactor cleansing following the run. An eighteen inch piece of 1/2" O.D. (0.120 wall) stainless steel tubing was welded between the liquefaction vessel and the bottom of the Y fitting. This length of tubing allowed the reaction vessel to be submerged into the heated sand bath, with limited radiative heat transfer to the other components of the system. The final branch of the Y fitting enables pressure monitoring as well as providing a route to the 1-liter system connections (see Figure 2). Pressure readings were recorded by a computer interfaced Bourne 0-5000 absolute pressure transducer. The use of quick connects leading to the 1-liter system connections and the specially machined Y fitting allowed the catalyst to be separately hydrided in the lower vessel prior to slurry addition. All 37° flared tubing connections were sealed with the appropriate crush washer to ensure no leaks occurred.

#### *Supporting equipment*

The Tecam fluidized sand bath (model SBL-2D) and its corresponding Techne TC-8D temperature controller were both manufactured in England, requiring special electrical modification to our laboratory. The English unit requires 220 VAC single phase power, while the U.S. standard incorporates 2 phases of 110 VAC to develop 220 VAC. Therefore, a Square D Company (catalog #5S7FIS) transformer was necessary before the sand bath was operational. The two microreactor units were mounted on a specially made aluminum reactor support attached to a Lab-Line Multi-Wrist Shaker. The shaker platform was attached to a 6' vertical piece of Thomson 60 case hardened and ground shaft by two custom designed combination bearing housings. The housings each had a 2-3/8" bore which enclosed both a Thomson ball bushing bearing (#A-203242) and a Thomson combination bearing (#CMB-1250). These bearings allowed linear and axial motion along the 1-1/4" O.D. shaft, respectively. A 36 kg counterweight was connected to the top of the shaker with a movable pulley system.

#### *PROCEDURES*

A specially manufactured tee fitting with an internal volume greater than 5 ml served as the microreactor. It was heated by the fluidized sand bath previously mentioned and monitored by a computer-interfaced pressure transducer. A catalyst sample was cleaned and hydrided in the microreactor, before a coal slurry was added to the vessel through a slant valve. Mixing was provided by the shaker attached to the microreactors. After reacting for a predetermined time span, the entire reactor system was lifted along a vertical shaft using linear bearings and a pulley system and rotated on axial bearings before being lowered into the quench tank. Venting, hydrogen, and vacuum lines were separately available for the slurry vessel and the microreactor.

#### *Catalyst preparation*

Prior to loading the reaction vessel with catalyst, it was necessary to seal one end of the tee by applying a thin coat of high stress lubricating compound to the threads and tightening the 37° flared tube cap. 0.2 g of catalyst was then placed in the reactor and the other end of the tee sealed

identically. Any excess anti-seize was removed to prevent sand from embedding in it when the reactor was lowered into the bath. The raw catalyst was then subjected to vacuum for 30 minutes to remove any physisorbed contaminants. Chemisorbed impurities were removed by exposing the alloy under investigation to a series of 6.9 MPa hydrogen treatments beginning at room temperature. Each exposure lasted approximately 4 h and was followed by evacuation for 30 min. After two room temperature cycles were completed, temperature was increased for single cycles at 93.3 and 204.4 °C and two cycles at 315.6 °C, before finally loading the catalyst matrix at room temperature. This stepwise conditioning process was used in order to remove surface contaminants without providing the necessary energy to produce more stable surface compounds.

#### *Microreactor operating procedures*

The general liquefaction procedure consisted of several steps. First, the coal slurries were prepared in the slurry reservoirs. The sand bath was regulated to the desired temperature and the slurries were added to the reaction vessels just prior to submerging the reactors in the sand bath. After the run was completed the reactors were removed from the sand bath and quenched in the water tank. Finally, the reactor contents were emptied for analysis and the reactors cleaned and dried for the next liquefaction runs.

The coal slurry was prepared by mixing 1.0 g of Alabama Black Creek coal (particle size 45-63 microns) with 2 ml of 1-methylnaphthalene and adding it to the slurry reservoir. Residual coal was then rinsed into the reservoir with an additional 3 ml of solvent. The reservoir contents were uniformly mixed and the vessel sealed by connecting the system tubing. The air atmosphere was removed by vacuum and a 5.5 MPa hydrogen overpressure established within the slurry vessel.

When the sand bath reached the desired temperature, the hydrogen pressure over the catalyst was reduced to 3.4 MPa and the slant valve was opened to deliver the coal slurry to the reaction vessel. The microreactors were then lowered into the sand bath and the shaker turned on to start the mixing. Additional hydrogen was added if necessary to establish a final operating pressure of 4.83 MPa. After a predetermined reaction time, the microreactors were removed from the sand bath and lowered into the cooling water quench tank using the vertical shaft and bearing system previously described. The reactor pressure was slowly reduced by venting with any trace gases being removed by a short vacuum treatment. The outside of the reactors were then dried by compressed air to remove any water before disassembly for product analysis and cleaning. One reaction vessel end cap was removed and the reactor contents rinsed into a 1-liter jar with tetrahydrofuran (THF). After the other cap was removed, both were cleaned with THF to deliver any reaction products remaining in the caps to the jar. The sample was then allowed to dissolve in 500 ml of THF for 24 h prior to filtration. The coal residue was rinsed from the slurry vessel and 0.12 inch walled tubing with THF and saved for filtration in order to determine how much coal was actually delivered to the reactors. After cleaning, compressed air was circulated through the microreactors to evaporate any residual THF. Finally, the reactor tee and end cap threads were cleaned to remove the anti-seize compound prior to using the reactor for the next run.

#### *Product analysis*

A modification of the pressure-filtration method described by Narain [16] was used to analyze the samples. Samples were contacted with 500 ml of THF and allowed to stand for 24 h prior to pressure-filtration through a glass microfiber prefilter and a 5-micron PTFE filter. An additional 500 ml of pure THF was pressure-filtered through the residue to complete the extraction. The filtrate was rotary evaporated to recover the THF for reuse. The remaining THF was allowed to evaporate from the concentrated product before repeating the procedure with two 500 ml aliquots of ethyl acetate. Filtration with cyclohexane completed the analysis. The weight of the dried insoluble

material from each filtration provided the product selectivity results.

#### DISCUSSION OF RESULTS

The samples obtained from the liquefaction runs were analyzed and the amounts of THF, ethyl acetate, and cyclohexane soluble materials were then used to calculate total conversion and product selectivity. All results were determined on a dry, ash-free (daf) basis.

Figure 3 shows conversion as a function of temperature for the liquefaction of 1 gram of Alabama Black Creek coal (45-63 microns) in 5 ml of 1-methylnaphthalene at 4.8 MPa. The runs were catalyzed by 0.2 grams of  $\text{CaNi}_5$  which was fully hydrided prior to the reaction. As can be seen in the figure, maximum yields of 21, 49, and 62% were achieved as the temperature increased from 315.6 to 426.7 °C. During noncatalyzed reactions under otherwise identical conditions, conversions of 18, 25, and 33% were obtained for the same temperatures of 315.6, 371.1, and 426.7 °C, respectively. This corresponds to the catalyzed conversion ranges of 20-30, 30-50, and 50-66% over the same set of temperatures. The trends in the 315.6 °C total conversion results follow the same trends reported previously [14] for the FeTi catalyst. Thus, the catalyst seems to be more effective as the temperature increases, which causes the alloy to release additional hydrogen from its matrix while improving the reaction rate. At higher temperature and longer reaction times we observed a decreasing overall conversion. This may be due to the total consumption of the internally stored hydrogen followed by repolymerization reactions which produce more THF insolubles.

Figure 4 shows the product selectivities for the catalysts studied at 426.7 °C and 4.83 MPa. The results for  $\text{CaNi}_5$ , FeTi,  $\text{LaNi}_5$ , and  $\text{Mg}_2\text{Cu}$  are depicted in Figures 4a, 4b, 4c, and 4d. Conversion can be obtained from these figures by subtracting the THF insolubles from 100%.  $\text{LaNi}_5$  appears to be the most active reaching its peak conversion after 30 minutes while the other three catalysts reach theirs after approximately 60 minutes.  $\text{CaNi}_5$ , FeTi, and  $\text{LaNi}_5$  all have conversions of 62-66 % with  $\text{Mg}_2\text{Cu}$  yielding only about 50 %. All the results show a maximum conversion, indicating that the hydrogen has been depleted from within the catalyst. Therefore, the free radicals are recombining to form larger molecules some of which are THF insoluble. This explains the large decrease in oil fractions compared to the preasphaltenes and asphaltenes.

Possible explanations for the trends observed with these catalysts can be found by examining both their desorption isotherms and their pure component catalytic hydrogenation properties.  $\text{LaNi}_5$ ,  $\text{CaNi}_5$ , and FeTi all have low temperature (25 °C) and low pressure (0.1-0.4 MPa) desorption isotherms and components with known hydrogenation activity. Thus, this combined effect must contribute to the higher conversions.  $\text{Mg}_2\text{Cu}$  has a high temperature (300 °C) and low pressure (0.5 MPa) desorption isotherm and metallic species with moderate hydrogenation activity. Preliminary results with  $\text{Mg}_2\text{Ni}$ , which also has a high temperature (300 °C) and low pressure (0.3 MPa) isotherm, show that the conversions are less than those obtained with  $\text{Mg}_2\text{Cu}$ . Thus, we conclude that the following series described the trends in activity for the catalytic hydrides studied to date:  $\text{CaNi}_5 - \text{LaNi}_5 > \text{FeTi} > \text{Mg}_2\text{Cu} > \text{Mg}_2\text{Ni}$ .

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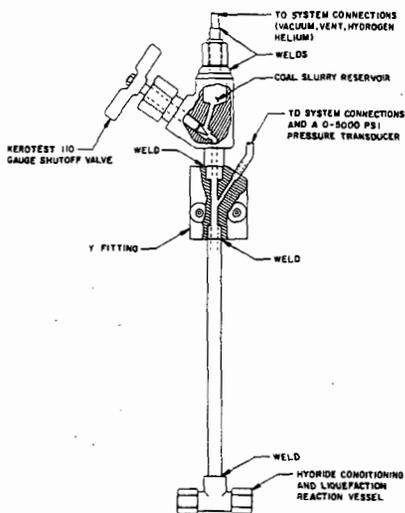


Figure 1. Schematic drawing of a microreactor unit.

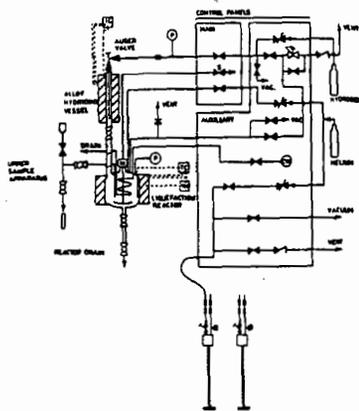


Figure 2. Method of interfacing the microreactor and 1-liter Autoclave system.

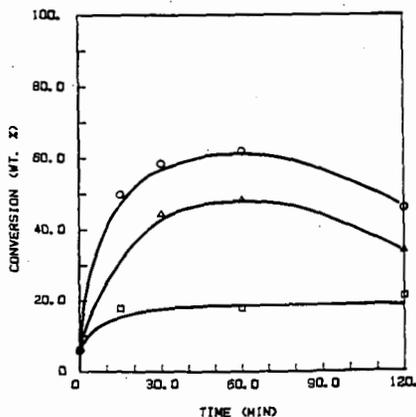


Figure 3. Conversion results for the liquefaction of 1 gram of Alabama Black Creek coal in 5 ml of 1-methylnaphthalene at 4.8 MPa using  $\text{CaNi}_5$  as a catalyst. [Key: (□) 315.6 °C; (△) 371.1 °C; (○) 426.7 °C]

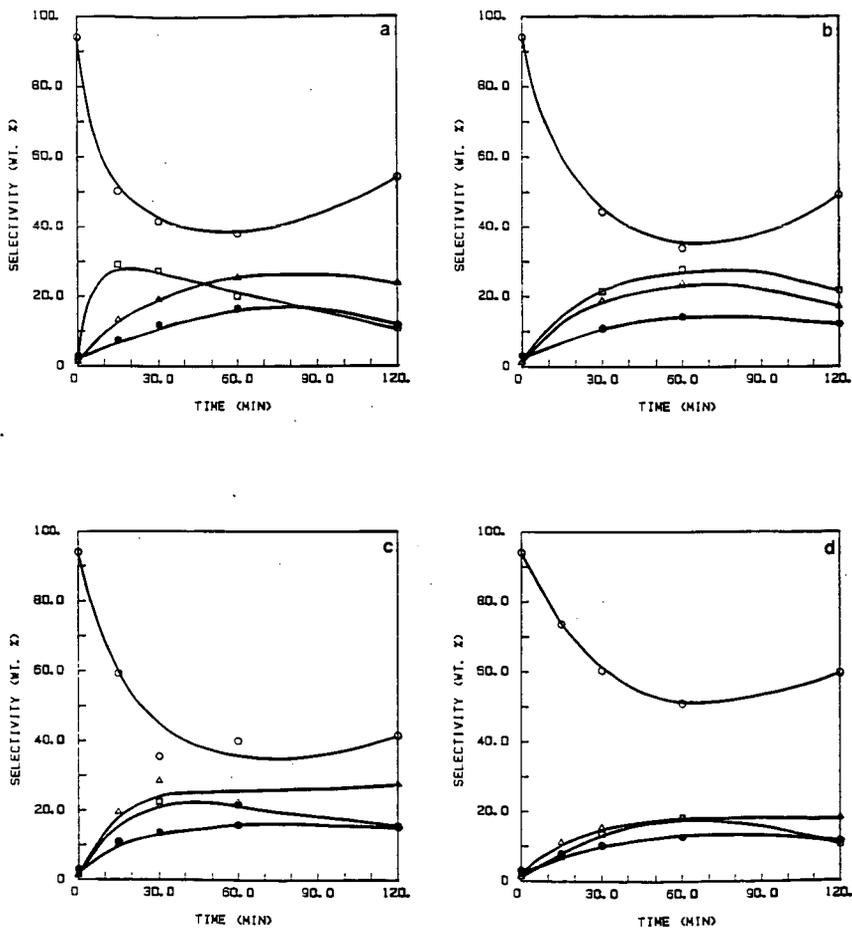


Figure 4. Selectivity results for the liquefaction of 1 gram of Alabama Black Creek coal in 5 ml of 1-methylnaphthalene at 426.7 °C and 4.8 MPa using the following catalysts: (a)  $\text{CaNi}_5$ ; (b)  $\text{FeTi}$ ; (c)  $\text{LaNi}_5$ ; and (d)  $\text{Mg}_2\text{Cu}$ . [Symbol key: ○ THF insolubles; Δ preasphaltenes; ● asphaltenes; □ oils].