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MASTER

DEVELOPMENT OF NEW CATALYSTS FOR
COAL-LIQUIDS REFINING

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FIRST QUARTERLY REPORT
for the period
1 January 1979 - 31 March 1979

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I. ABSTRACT

Two existing hydrotreating units were redesigned to increase their operating range, and the necessary parts ordered. A new microactivity testing (MAT) unit was designed, and the parts ordered.

Base-line testing procedures were improved, and the effect of unit parameters on catalytic activity was studied with borrowed Filtrol testing units.

Synthesis and characterization of various catalytic components and matrix modifications was carried out. Sodium-Y zeolites with different silica-alumina ratios and different crystal sizes are being synthesized. Synthetic montmorillonite micas (SMM) in the ammonium (SMM-NH₄) form have been prepared with silica-alumina ratios from 2.16 to 2.58, and cation exchanged with Co and Ni. Lattice-substituted SMM (SMM-M) have been prepared on a laboratory scale with Ni²⁺, Co²⁺, and Fe³⁺ substituted for Al³⁺ in the octahedral coordination position.

A series of relatively large pore size alumina supports with varying pore size distributions, and good strengths, have been prepared. These alumina supports have been made into hydrotreating catalysts by impregnation with different concentrations of CoO/MoO₃ and NiO/MoO₃.

II. OBJECTIVE AND SCOPE OF WORK

The objective of this project is to develop catalysts that will be more active and selective and longer-lived than present commercial catalysts under the process conditions necessary for the efficient conversion of coal-derived syncrude to gasoline and other distillate fuels in current types of catalytic cracking and hydrotreating units. The feedstocks to be processed are: a 350 - 850°F blend of SRC II product distillate, and a hydrogenated product from this feed material with a hydrogen content of 10.5 - 11.0%.

The approach will be to prepare and test catalysts that are likely to be effective with polynuclear aromatics and with high concentrations of sulfur and nitrogen compounds. This will entail preparing catalysts with high activity, thermal stability, resistance to poisoning by nitrogen compounds, and large pores to permit diffusion of large molecules. Hydro-treating, hydrocracking, and cracking catalysts will be prepared and tested. The catalysts will include numerous preparations of catalytic components such as exchanged and impregnated zeolites as well as exchanged and lattice-substituted synthetic montmorillonite micas utilizing catalytically active metals such as cobalt, molybdenum, nickel, chromium, platinum, palladium, iron and manganese, impregnated large pore supports such as aluminas and silica-aluminas, and combinations of superior catalytic components and support materials. They will be tested to establish their activity as hydrogenation catalysts (for aromatic substitution, heteroatom removal, hydrocracking) and as cracking catalysts (for conversion of high boiling feed into low boiling liquid products).

III. SUMMARY OF PROGRESS TO DATE

During the quarter the following tasks have been undertaken. These tasks are listed in the Milestone Chart in Figure 1. Detailed discussion of technical progress is found in the next section.

Task I - Modification and Building of Test Units

Two existing hydrotreating units were redesigned to improve run reproducibility, and to increase the operating range of the units. Commercially available parts have been ordered, and design drawings submitted to fabricators. A new microactivity testing unit (MAT) has been designed, and the majority of the parts ordered.

Task II - Base-Line Data and Test Procedures

The MAT test procedure is being improved. A new glass feed preheater system is being tested in place of the traditional metal block type. Product gas collection has been switched from a wet method (over water) to a dry-bag system.

Hydrotreating base-line data on the effect of unit parameters on catalytic activity are being obtained with Filtrol units. A commercial hydrotreating catalyst, Filtrol HPC-6, and a Kuwait vacuum gas oil are being used until the PAMCO SRC II Fuel Oil blend is received.

Task III - Modification of Catalytic Component

Laboratory procedures are being developed to synthesize sodium-Y zeolites with normal, 1-8 μ , crystal size. Synthetic montmorillonite micas (SMM) in the ammonium form have been obtained in pilot plant batches with silica-alumina ratios from 2.16 to 2.58. Lattice substituted SMM have been prepared on a laboratory scale with Ni^{2+} , Co^{2+} , and Fe^{3+} substituted for Al^{3+} in the octahedral coordination position.

Task IV - Cation Exchange

Ammonium-SMM have been exchanged with $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ on a laboratory scale.

Task V - Matrix Modification

A series of relatively large pore size alumina supports with varying pore size distributions, and good strength, have been obtained. The physical properties of these materials have been determined.

Task IX - Hydrotreating Catalyst Preparation

Three alumina supports with Kaiser SA alumina to Condea SB alumina ratios of 80/20, 23/77, and 80/20 + TiO_2 were each impregnated with three different CoO/MoO_3 , and three different NiO/MoO_3 concentrations of metals in pilot plant amounts.

FIGURE 1. MILESTONE CHART

Remarks: * Delay in start of Task due to patent waiver contract negotiations.

▽ Intermediate Event

△ Major Milestone

◇ Approved Change

IV. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

A. Task I - Modification and Building of Test Units

1. Modification of Hydrogenation Units

During the first quarter of 1979, existing hydrotreating units were redesigned to improve run reproducibility, and to increase the operating range of the units. Essentially all of the commercially available components are in the process of being ordered for upgrading two units for hydrotreating and hydrocracking catalyst activity testing. Requests for quotations have been submitted, and quotations have been received and competitively evaluated. Orders have been placed, and deliveries are being received. Specifications and drawings have been submitted to fabricators for the construction of reactor tubes, and the exit gas-liquid separators for these units.

2. Construction of Microactivity Testing (MAT) Unit

A site for the new cracking unit was set aside within the laboratory and cleared of the existing equipment.

The unit has been designed with furnaces and facilities for two catalytic reactors. The feed and product lines are controlled by solenoid valves with the option of manual operation or automatic sequencing of the valves under computer control. The reactor furnaces are three-zone with temperature control of each zone and independent control of the feed inlet preheat line during the reaction cycle.

Requests for quotations on essentially all components for this unit have been initiated. At least 95 percent of the quotations have been received and evaluated and appropriate orders have been placed. Deliveries are starting to be made with delivery of the last major item, the reactor furnaces, expected in early May.

B. Task II - Base-Line Data and Test Procedures

In order to make up time lost because of a three-month delay in the actual start of contract work, due to patent waiver contract negotiations, it was decided to utilize existing Filtrol units to carry out this task instead of waiting until the modified, and new units of Task I are ready.

1. Cracking and Hydrocracking

During the first quarter of 1979, research using Filtrol's microactivity unit was directed toward improving the versatility and reliability of the microactivity test method. The microactivity

test itself is a rapid method of measuring basic catalyst properties including conversion, coking, and gas make. Qualitative information on product selectivity can also be obtained.

The major component of the microactivity unit is a glass reactor inserted in a tubular furnace (see Figure 2). Feed is injected by a syringe pump through a deadman preheater into the reactor. A thin vycor layer further preheats and disperses the feed before it contacts a fixed catalyst bed, which rests on a pyrex wool support. An automatically actuated four-way valve regulates the on-stream time of the feed. The liquid cracking product, or syncrude, is trapped in a calibrated receiver and the gaseous products flow to a collection system. Both liquid and gases are analyzed by gas chromatography.

To accomplish the objectives of the present project, several improvements must be made in the micro unit. In particular, modifications of the feed preheater, and a workable technique for dry gas sampling are needed. These are the areas of current research.

Historically the feed preheater in the microactivity unit consisted of a metal block fitted into the reactor body. The block, or "deadman," contained 34 inches of coil in which the feed was vaporized before contacting the catalyst bed. The long residence time of feed vapors in the coil promotes thermal cracking of the heavier components. The use of different feedstocks also leads to problems in maintaining a fixed vapor temperature. Since the metal deadman provides a constant amount of preheat independent of feed composition, lighter feeds are emitted at a higher temperature than heavier ones. Extremely heavy feeds may not even vaporize completely. Data collected from microactivity tests employing identical catalyst and feedstock (Figure 3) show that conversion is sensitive to feed temperature. Clearly the metal deadman is inadequate for the present purposes.

Currently a new glass deadman is being tested as a possible solution to the preheater problem (see Figure 4). The coil of the metal deadman is replaced with a syringe needle housed in pyrex tubing. The needle is connected in series with a controller/transformer, making a resistance heater. The control thermocouple is positioned just below the needle tip, so the instantaneous vapor temperature at the needle outlet determines the amount of current supplied to the needle. A second thermocouple measures temperature in the catalyst bed.

The glass deadman is more versatile than its metal predecessor. The controller provides sufficient current to heat the feed to a predetermined set point (usually 900°F), regardless of feed composition or flow rate. A second advantage is the shorter residence time of vapors in the heated needle as compared to the longer coil. This aids not only in eliminating thermal cracking of the feed, but also reduces lag time between injection and actual contact of the feed with the catalyst.

FIGURE 2. MICROACTIVITY TEST UNIT

FIGURE 3 Cracking Conversion vs. Feed Temperature

FIGURE 4. GLASS DEADMAN ASSEMBLY

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Progress has also been made in the area of product gas collection from the microactivity unit. One objective of the project is to analyze the gaseous product for hydrogen sulfide content, in addition to hydrogen and the light hydrocarbons. The present method of collecting gas over water (wet method) is unacceptable, since H_2S is soluble in water to an appreciable extent. For²this reason, a dry gas collection system has been devised. The gases are charged to an evacuated, leak-proof bag which is weighted down and totally submerged in a calibrated beaker. The volume of the gas produced is obtained simply by noting the change in the liquid level that occurs during the run. Sample bags can then be removed and stored for later GC analysis.

A third modification of the microactivity unit is the addition of a filter in the product gas line. During the post-run stripping period unreacted feed becomes entrained in the helium strip gas and is eventually deposited in the gas collection system. This heavy carbonaceous residue absorbs some lighter hydrocarbons resulting in misleading gas analyses, and also contributes a small but noticeable error in the material balance. Left unchecked, accumulated deposits may eventually cause mechanical failure of in-line solenoid valves. To eliminate these problems, a simple removable filter has been placed in the gas line prior to the gas collection system.

2. Hydrotreating

a. Introduction

Filtrol hydrotreating units are being used to develop test procedures for use with the SRC II Fuel Oil Blend. Base-line data on the effect of unit parameters on catalytic activity are being obtained with a commercial hydrotreating catalyst, Filtrol HPC-6.^(a) A petroleum feedstock, Kuwait vacuum gas oil VGO, 2.7% sulfur, is being used in the absence of the coal liquid feed, which we have not yet received. The data from a petroleum feedstock will also provide a useful basis for comparing the performance of the modified equipment, with a commercial catalyst, on both a petroleum feedstock and the coal liquid feed.

b. Experimental

The catalyst 100 ml, diluted with 200 ml of sand,^(b) is charged to the reactor (Figure 5), and the system is slowly raised to temperature with feed and H_2 flowing. After temperature is reached, the catalyst is presulfided by the feed for eight hours before any points are taken. Points are then taken at intervals, and analyzed for sulfur and nitrogen content.

^(a) 15% MoO_3 , 4% CoO ; on γ -alumina, 1/16"; SA = 230 m^2/g , PV = 0.59ml/g.

^(b) Crystal silica sand, 30 mesh.

FIGURE 5. HYDROTREATING ACTIVITY TEST SYSTEM

c. Results and Discussion

Preliminary results on the effect of temperature, pressure, and H_2 /feed on desulfurization are presented in Figures 6 - 8. ² (Hydrodenitrogenation results are pending.) At 690°F, and 2 LHSV increasing the pressure above 800 psi, or the H_2 /feed flow ratio above 1500 SCF/BBL does not increase the percent desulfurization of the VGO feed. Within the 650-750°F temperature range, hydrodesulfurization appears to vary between 80 and 95% as an almost linear function of temperature.

d. Future Work

We expect to receive the SRC II Fuel Oil Blend in the near future, and will carry out base-line hydrotreating activity tests on this feed at a series of different run conditions (temperature, pressure, space velocity) to establish optimum run conditions for subsequent testing of new catalysts prepared in the course of this contract.

C. Task III - Modification of Catalytic Component

1. Faujasite Modification

a. Introduction

Although FCC feedstocks derived from coal will have been subjected to one or more hydrogenation steps, they will be more aromatic, contain more condensed rings, and have a higher nitrogen content than petroleum-derived feedstocks (1). This means that they will require higher temperature cracking and produce more coke. This, in turn, can require longer temperature regeneration to insure burning off coke to a sufficiently low level. The thermal stability of cracking catalysts with faujasite-type zeolite as the active component is enhanced by reducing the soda content to low levels, raising the zeolite silica-alumina ratio, and, to a lesser extent, by having rare earth ions present. The catalytic activity of the zeolite results from the presence of acid sites, which are more acidic but less numerous as the silica-alumina ratio increases. It is these sites that are poisoned by nitrogen bases; however, because the poisoning occurs through formation of dissociable, substituted ammonium salts of solid acid, one would expect lower adsorption of nitrogen base at higher temperatures and, thus, greater retention of catalytic activity. To take advantage of this phenomenon, the zeolite must be thermally stable. Consequently, catalysts to be tested will be based on zeolite that is highly stable, consistent with retention of a high degree of catalytic activity.

FIGURE 6. DESULFURIZATION VS. TEMPERATURE

FIGURE 7. DESULFURIZATION VS. PRESSURE

FIGURE 8. DESULFURIZATION VS. H_2 FLOWRATE

Use of feeds with large polycyclic molecules means that cracking can become diffusion limited in the matrix and in the zeolite crystal. This would result in longer residence times within the catalyst and consequent overcracking to coke, which exacerbates the problem by limiting diffusion even more. Two approaches to minimize this are to use a matrix with large pores and to decrease the diffusion path length in zeolite crystals by compounding the catalyst with finely divided zeolite crystals such as have been described in the literature. Both of these approaches will be explored.

b. Experimental

(1) Preparation of Na-Y Zeolite (normal, 1-8 μ , crystal size) with silica-alumina ratio greater than 5

The procedure employed was the same as that described by Breck (2). Sodium aluminate (136g) was added to water (540g) with rapid stirring. Sodium hydroxide (64.7g) was then added to the slurry. Additional heat was applied to the mixture until a tan-colored solution was obtained. After cooling to room temperature, during which time a small amount of precipitate formed, the solution was added to a rapidly stirred ammonium-stabilized silica sol (LUDOX, 780g, VF = 39.5). After stirring briefly (10 minutes) to obtain a homogeneous mixture, the white gel of molar composition $2.4 \text{ Na}_2\text{O}:\text{Al}_2\text{O}_3:8 \text{ SiO}_2:96\text{H}_2\text{O}$ was allowed to digest at room temperature for 24 hours and then subjected to 100°C until the XRD pattern showed that the sample had reached 100% crystallinity (2 days).

(2) Preparation of Na-Y Zeolite (small, <1 μ , crystal size) with silica-alumina ratio greater than 5

The procedure employed was identical to that described above for the preparation of normal crystal size zeolite except for two changes as adapted from a patent by Maher and Scherzer (3). The sodium hydroxide-sodium aluminate solution was filtered to remove all solid matter and then cooled to 4°C prior to addition to the LUDOX which was also cooled to 4°C. After the 24-hour room temperature digestion, methanol (15 ml) was added to one-half (500 ml) of the reaction mixture. Both slurries were then heated at 100°C until maximum crystallinity (97%) was obtained (4½ days).

c. Results and Discussion

Following the procedure outlined by Breck (2) for the synthesis of a Type-Y Zeolite of silica-alumina ratio greater than 5, we obtained a 100% crystalline type-Y zeolite of silica-alumina ratio 5.4, as determined by XRD and elemental analyses.

Preparation of a small particle size zeolite of silica-alumina ratio greater than 5 was attempted by a modification of the above procedure as suggested by Maher and Scherzer (3). The alumina solution was both filtered and cooled to 4°C along with the silica source (LUDOX) before mixing. Methanol was added to half of the mixture to improve crystallinity. The material obtained, however, was essentially identical to the zeolite produced in the first procedure. The silica-alumina ratio was 5.4, the material was 97% crystalline, and the particle size, as determined by x-ray, was the same or larger than the particle size obtained above.

A possible explanation for the failure of this procedure to produce small particle size zeolite lies in the concentration of reactants used. The Maher and Scherzer (3) preparation of small particle size Type-X zeolite required very dilute solutions in conjunction with the cold temperature and organic solvent. Our method included the cold temperature and organic solvent but employed a more concentrated reaction mixture, as is typical for the preparation of Type-Y zeolite.

d. Work Forecast

During the next Quarter, pilot plant scale preparation of normal crystal size Na-Y zeolite will be carried out. When this is completed, a portion of this material will be used to produce Na-Y zeolite with a silica-alumina ratio of approximately 8.

Additional laboratory work will be carried out to produce small crystal size Na-Y zeolite. More dilute reaction mixtures will be used in the preparations.

2. Synthetic Montmorillonite Mica (SMM) Modification

a. Introduction

Synthetic mica-montmorillonite (SMM), a laminar 2:1 layer-lattice aluminosilicate, was first synthesized by Granquist (4). SMM has the general unit cell formula for the ammonium form given below

where the superscripts "oct" and "tetra" refer to atoms having octahedral and tetrahedral coordination respectively. SMM clays are classified as dioctahedral or trioctahedral, depending upon whether the number of lattice cations per unit cell in the octahedral (or inner) layer is approximately 4 or 6 (all positions filled), respectively. The formula above refers to a dioctahedral clay.

SMM shows catalytic cracking activity and the available data shows that SMM, although not as active as zeolitic catalysts, is much more active than amorphous silica-alumina (5). SMM would also be expected to be an excellent matrix material. The use of SMM as a support for hydrogenation metals has also been patented. Csicsery and co-workers (6,7) demonstrated the activity of Pd-SMM, Pd-SMM-zeolite composites, and Pd-SMM-M (M represents low concentrations of other metals such as Mn, Cr, Fe, W, Mo, Co, etc.) for hydrocracking.

We are therefore preparing SMM in the ammonium form with a range of silica-alumina ratios. These materials will be tested as cracking catalysts after deamination. They will also be used as matrix materials, and as components in hydrocracking and hydrotreating catalysts after exchange and impregnation.

b. Experimental

The general procedure for preparing SMM is as follows (4):

Ingredients are thoroughly mixed in a pilot plant Cowles mixer until the resultant slurry is homogenous and without lumps. The slurry is then charged to a high pressure autoclave equipped with a high speed stirrer (Magne-drive-Autoclave Engineers). The reaction temperature is raised, and autogeneous steam pressure from the slurry is obtained, and maintained for the time indicated. Upon completion of the run, heating is discontinued and the slurry is removed under pressure (temp. $\sim 250^{\circ}\text{F}$). In most cases the product slurry is sheared with a high speed Cowles mixer and spray dried.

The charge ingredients and run conditions are presented in Table I, and the charge and product mole ratios, along with the % mica, in Table II.

c. Results and Discussion

Five large scale pilot plant batches of SMM ranging from 26-37 kg each were produced with silica-alumina ratios from 2.16 to 2.58. These materials are available for testing as cracking catalysts. The most active SMM will also be tested in mixtures with zeolites and other matrix modifications for cracking activity. The SMM with silica-alumina ratios of 2.16 and 2.58 are being exchanged with nickel and cobalt to produce hydrocracking and hydrotreating components (Section IV-D-1).

TABLE I. PREPARATION OF SMM - CHARGE INGREDIENTS AND RUN CONDITIONS

-----Charge Ingredients (Parts dry wt.)-----							-----Run Conditions-----				
Sample	PSA ^(a)	Gibb. ^(b)	m-Kaolin ^(c)	NH ₄ ·HF	NH ₄ OH ^(d)	H ₂ O	Run Time ^(e)	Pressure	Temp.	pH(in)	pH(out)
2	3.00	1.00	19.95	0.32	1.96	179.0	4 hrs.	1240 psig	572°F	7.8	6.65
3	4.07	1.00	19.11	0.67	1.42	165.1	12 hrs.	1240 psig	600°F	8.3	5.93
4	5.25	1.00	19.11	0.73	1.16	153.2	15 hrs.	1240 psig	675°F	8.1	5.7
1	6.65	1.00	19.88	0.81	0.93	139.6	12 hrs.	1240 psig	575°F	7.2	--
5 ^(f)	6.42	1.00	19.10	0.78	0.89	138.53	15 hrs.	1240 psig	675°F	7.3	6.0

(a) PSA (polysilicic acid) - 5.5-6.0 wt. % SiO₂ in water, obtained by passing dilute sodium silicate solution through an acidified (H₂SO₄) ion exchange resin.

(b) Gibb. (gibbsite alumina) - Alcoa C-31 (65% solids).

(c) m-Kaolin (meta-kaolin) - Freeport Al-Sil-Ate OP (100% solids).

(d) NH₄OH (ammonia solution) - 28% NH₃

(e) Does not include heat-up time — usually about 4 hours.

(f) Contains "seed" SMM from previous run (~ 2% on dry basis).

TABLE II. PREPARATION OF SMM - CHARGE AND PRODUCT MOLE RATIOS

Sample	---Charge Mole Ratios---			--Product Mole Ratios--		
	$\text{SiO}_2/\text{Al}_2\text{O}_3$	$\text{NH}_4/\text{Al}_2\text{O}_3$	F^-/SiO_2	$\text{SiO}_2/\text{Al}_2\text{O}_3$	$\text{NH}_4/\text{Al}_2\text{O}_3$	% Mica ^(a)
2	2.2	.600	.050	2.16	0.44	70
3	2.4	.532	.100	2.28	0.43	64
4	2.6	.467	.100	2.45	0.41	58
1	2.8	.400	.100	2.51	0.39	(32)
5	2.8	.400	.100	2.58	0.41	52

^(a)Determined by XRD method similar to that in Ref. (4).

3. Lattice-Substituted SMM (M-SMM)

a. Introduction

The charge requirement of SMM may also be met by six divalent ions, such as Ni^{2+} , Co^{2+} , and Mn^{2+} , as well as by other trivalent metals such as Fe^{3+} (5). These ions, because of their size and charge, substitute for Al^{3+} in the octahedral coordination position. If all the octahedral positions are filled, the resultant material is called a trioctahedral clay. Mixtures of di- and trioctahedral clays can also be obtained if less than stoichiometric substitution occurs.

These lattice-metal-substituted SMM's (M-SMM) show a substantial increase in activity relative to SMM in hydrocracking and hydroisomerization studies. In one study (8) involving hexane hydrocracking the data shows an increase in activity with increasing Ni concentration (Ni^{2+} substituted for Al^{3+} in the octahedral layer) with the highest activity corresponding to 5 Ni atoms per unit cell. A study (9) involving hexane hydroisomerization not only shows a dramatic activity increase for Ni-SMM relative to SMM but also increased formation of 2,2-dimethylbutane as the Ni content increases from 0 to 5 Ni per unit cell. Incorporation of cobalt into the SMM lattice also results in increased hydrocracking activity relative to SMM, although not as extensive as for Ni-SMM with the same amount of substitution (10). Generally for the above studies a hydrogenation component such as Pd is impregnated on the M-SMM prior to use by established ion exchange techniques.

Filtrol is therefore synthesizing M-SMM with four metals (Ni, Co, Fe, Mn) at different concentrations (7% and 14%) for testing as components of hydrocracking and hydrotreating catalysts.

b. Experimental

According to a previously published procedure (8), the following M-SMM's have been prepared:

- (1) Ni-SMM. To a rapidly stirred solution of 2127.0g, SSB (ammonium stabilized polysilicic acid) was added 120.0g $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ (Alcoa C-31) and 6.1g $\text{NH}_4\text{F} \cdot \text{HF}$. An ammoniacal slurry of 100g H_2O , 20.1g NH_4OH (58%), and 161.0g $\text{Ni}(\text{CH}_3\text{CO}_2)_2 \cdot 4\text{H}_2\text{O}$ was then added to the silica-alumina slurry, resulting in the immediate formation of a gel. Water was then added to break down the gel. The resulting slurry was 8.7% VF solids. Approximately 63% of the above was introduced into a one-gallon autoclave which was then heated to 285°C over a 3-hour period until the pressure lined out at 1000 psi. The autoclave was maintained at that temperature for ca. 12 hours. During

the run, samples were taken at 2 and 5 hours after lining out. At the end of the run the autoclave was purged of the remaining Ni-SMM slurry by steam pressure. Prior to analysis, the samples were washed with water and dried at 100°C.

- (2) Co-SMM. Co-SMM was prepared in the one-gallon autoclave in a similar manner to Ni-SMM with the use of the following quantities of starting materials: 1592.5g SSB (5.63% SiO_2); 90.0g $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ (Alcoa C-31); 4.6g $\text{NH}_4\text{F} \cdot \text{HF}$; 120.9g $\text{Co}(\text{CH}_3\text{CO}_2)_2 \cdot 4\text{H}_2\text{O}$; 15.6g NH_4OH (58%); and enough water to give a slurry containing 10.0% VF solids. The autoclave lined out at 285°C and P = 1100 psi after 2.5 hours of heating. A sample was withdrawn 1 hour after lining out. A leak was noted at 1 hour and 45 minutes after lining out, the heat turned off, and the Co-SMM slurry purged from the system under steam pressure. Prior to sample analysis, the solid was washed with water and dried at 100°C.
- (3) Fe-SMM. To 622.6g SBB (5.63% SiO_2) was added 35.0g $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ (Alcoa C-31) and 1.8g $\text{NH}_4\text{F} \cdot \text{HF}$ in succession while stirring. An ammoniacal slurry consisting of 60 ml H_2O , 35.5g $\text{Fe}(\text{OH})(\text{CH}_3\text{CO}_2)_2^a$, and 10.3g NH_4OH (58%) was then added to the above silica-alumina slurry. The gel which formed was broken upon the addition of 75 ml water. The resulting slurry was 11.3% VF solids. The slurry was poured into a 2ℓ autoclave (Parr) and heated up to 284°C during a three-hour period. Heating was maintained at $287 \pm 12^\circ\text{C}$ over the next four hours after which time the autoclave was cooled to ambient temperature. The x-ray diffraction (XRD) pattern discussed in the results section below corresponds to crude, unwashed product.

c. Results

- (1) Ni-SMM. A comparison of XRD spectra for the material heated at 285°C for 12 hours vs. the 2-hour sample shows that crystal formation was essentially complete within 2 hours. The Ni-SMM prepared here gives an XRD pattern similar to that previously reported (8). The formation of mixed phase material upon Ni^{+2} substitution in the lattice is readily apparent in the XRD spectrum which exhibits the trioctahedral (06)(1.523Å) and dioctahedral (06)(1.500Å) reflections having essentially equal intensities (42 mm tri/46mm di) consistent with approximately 2 Ni atoms per unit cell. The pale green solid contains 14.8% Ni on a VF basis and a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 2.18.

^aThe $\text{Fe}(\text{OH})(\text{CH}_3\text{CO}_2)_2$ used in the prep. has since been found to contain ca. 14% Fe metal. Thus the prepared Fe-SMM contains Fe impurity.

- (2) Co-SMM. A comparison of XRD spectra for the 1 hour sample and that of the remaining bulk material shows the latter spectrum possesses slightly greater peak height intensities (but on the order of the noise level) and slightly greater peak resolution. The XRD pattern is similar to Ni-SMM prepared above, and the trioctahedral ($1.534\text{\AA}$) and dioctahedral ($1.505\text{\AA}$) reflections are of essentially equal intensities (17mm di/19mm tri) indicating that the Co content is approximately 2 Co atoms per unit cell or 14%. The solid is pink in color. Chemical analyses are pending.
- (3) Fe-SMM. The rust colored solid gives an XRD pattern similar to the other M-SMM's except that no trioctahedral reflection is observed in the Fe case. A dioctahedral reflection ($1.502\text{\AA}$) is seen only. Chemical analyses are pending.

d. Discussion

The above work shows that the Ni-, Co-, and Fe-SMM clays can indeed be synthesized, as would be expected (11), and the general conditions and techniques have been established.

The (06) reflection in the XRD spectrum is particularly diagnostic relative to the amount of metal lattice substitution. The Ni and Co clays exhibit reflections for both dioctahedral and trioctahedral phases consistent with the substitution for trivalent aluminum by divalent Co or Ni. The formation of a trioctahedral phase is a result of the need for increased metal ion substitution in the lattice to offset the increased negative charge as one goes from tri- to divalency. It is therefore not particularly noteworthy that Fe-SMM exhibits only a dioctahedral phase since the substituting iron is trivalent. Furthermore, unlike the Co and Ni cases, Fe-SMM may contain Fe ion in the tetrahedral layers since its ionic radius ($0.64\text{\AA}$) is equal to the maximum ($0.64\text{\AA}$) (11), able to fit in those sites.

e. Work Forecast

During the next Quarter, laboratory scale preparations will be carried out to synthesize the Mn-SMM at the 14% metal level, and also to produce M-SMM at the 7% level for M = Ni, Co, Fe, and Mn.

The preparations will then be scaled up to pilot plant quantities with the use of a 10-gallon autoclave unit.

D. Task IV - Cation Exchange

1. SMM Exchange

a. Introduction

As discussed earlier (Section IV-C-2), NH_4 -SMM have been prepared for a variety of applications. Two of these SMM modifications with different silica alumina ratios are to be cation exchanged with cobalt and nickel to produce Ni- and Co-SMM for use as components of hydrocracking and hydrotreating catalysts.

b. Experimental

In order to optimize the exchange process, the exchanges were done on a bench scale, using $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ as exchange salts and varying different exchange parameters in the exchange process. In order to find the optimum salt/SMM ratio, the exchanges with each metal were carried out at several different metal dosages ranging from 0.1 to 1.3g salt: 1 VF g SMM: 10g H_2O . The water added was adjusted to allow for the water content in the salt and SMM. The pH of the exchange slurry was consistently ~ 6 .

The effect of exchange temperature was investigated by carrying out exchanges at room temperature and at 90°C , for one hour each. In order to establish if preliminary calcination of the starting material has any effect upon its exchange capability, several SMM samples were calcined at 800°F prior to ionic exchange. The products obtained from all these exchanges were water washed, dried at 105°C and analyzed. Analytical data for the starting materials as well as for some of the exchange products are given in Tables III and IV.

c. Results and Discussion

The data show that filter cakes have a better exchange capacity than spray dried materials. They also show that the use of 0.5g salt per gram of SMM results in the same metal input (about 1.5 wt. % metal) as the one achieved with higher salt/SMM ratios.

An increase in exchange temperature to 90°C under otherwise identical conditions, increases the metal input into the SMM from 1.5% to 1.7%.

d. Future Work

As soon as all analytical data become available, we will be able to optimize the exchange process of SMM. Using the optimized procedure, we plan to make 10 kg of Co- and Ni-exchanged SMM, respectively, in the pilot plant. Filter

TABLE III. EXCHANGE OF SPRAY-DRIED NH_4 -SMM^(a) WITH
 $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}^{(b)}$ and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}^{(b)}$

Spray-Dried SMM + $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$

Product Mole Ratio								
<u>n</u>	<u>T(°C)</u>	<u>$\text{SiO}_2:\text{Al}_2\text{O}_3:\text{Na}_2\text{O}:\text{NH}_3:\text{Fe}_2\text{O}_3:\text{CoO}$</u>						<u>% NH_3</u>
0.1	25	2.40	1	.004	.005	.04	.92	
0.3	25	2.40	1	.003	.005	.05	1.15	
0.5	25	2.40	1	.003	.32	.005	.06	2.19
1.0	25	2.40	1	.003	.31	.005	.06	2.13
1.3	25	2.40	1	.003	.31	.005	.06	2.11
1.0	25 ^(c)	2.40	1	.013	.14	.005	.06	.95

Spray-Dried SMM + $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$

Product Mole Ratio								
<u>n</u>	<u>T(°C)</u>	<u>$\text{SiO}_2:\text{Al}_2\text{O}_3:\text{Na}_2\text{O}:\text{NH}_3:\text{Fe}_2\text{O}_3:\text{NiO}$</u>						<u>% NH_3</u>
0.1	25	2.40	1	.004	.004	.04	.88	
0.3	25	2.40	1	.003	.004	.04	1.01	
0.5	25	2.40	1	.003	.33	.004	.05	2.27
1.0	25	2.40	1	.003	.31	.004	.05	2.15
1.3	25	2.40	1	.003	.32	.005	.05	2.18
1.0	25 ^(c)	2.40	1	.012	.16	.005	.05	1.07

(a) SMM: $2.40\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot 0.02\text{Na}_2\text{O} \cdot 0.46\text{NH}_3 \cdot 0.005\text{Fe}_2\text{O}_3$

(b) Stoichiometry: 1VfgSMM:ngSalt:10gH₂O

(c) SMM calcined at 800°F for 3 hours prior to exchange.

TABLE IV. EXCHANGE OF WET-CAKE $\text{NH}_4\text{-SMM}^{(a)}$ WITH
 $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}^{(b)}$ and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}^{(b)}$

<u>Wet Cake SMM + $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$</u>									
Product Mole Ratio									
<u>n</u>	<u>T(°C)</u>	<u>$\text{SiO}_2:\text{Al}_2\text{O}_3:\text{Na}_2\text{O}:\text{NH}_3:\text{Fe}_2\text{O}_3:\text{CoO}$</u>						<u>% Co</u>	<u>% NH_3</u>
0.1	25	2.43	1	.002		.005	.044	1.02	
0.3	25	2.43	1	.002		.005	.054	1.26	
0.5	25	2.43	1	.002	.23	.004	.06	1.49	1.56
1.0	25	2.43	1	.001	.23	.004	.06	1.51	1.54
1.3	25	2.43	1	.001	.21	.004	.06	1.51	1.45
1.0	25 ^(c)	2.43	1	.007	.12	.004	.06	1.39	.80
0.1	90	2.43	1						
0.3	90	2.43	1						
0.5	90	2.43	1	.001		.005	.07	1.64	
1.3	90	2.43	1	.001		.005	.07	1.71	

<u>Wet Cake SMM + $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$</u>									
Product Mole Ratio									
<u>n</u>	<u>T(°C)</u>	<u>$\text{SiO}_2:\text{Al}_2\text{O}_3:\text{Na}_2\text{O}:\text{NH}_3:\text{Fe}_2\text{O}_3:\text{NiO}$</u>						<u>% Ni</u>	<u>% NH_3</u>
0.1	25	2.43	1	.002		.005	.05	1.14	
0.3	25	2.43	1	.002		.005	.06	1.37	
0.5	25	2.43	1	.002	.23	.005	.06	1.41	1.56
1.0	25	2.43	1	.002	.24	.005	.06	1.39	1.64
1.3	25	2.43	1	.002	.22	.005	.06	1.42	1.51
1.0	25 ^(c)	2.43	1	.008	.12	.004	.06	1.30	.79
0.1	90	2.43	1						
0.3	90	2.43	1						
0.5	90	2.43	1	.001		.005	.07	1.59	
1.3	90	2.43	1	.002		.005	.07	1.63	

(a) SMM: $2.43\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot 0.013\text{Na}_2\text{O} \cdot 0.37\text{NH}_3 \cdot 0.005\text{Fe}_2\text{O}_3 \cdot 0.005\text{Fe}_2\text{O}_3$

(b) Stoichiometry: 1VFgSMM:ngSalt:10gH₂O

(c) SMM calcined at 800°F for 3 hours prior to exchange.

cake SMM, with low and high $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios, will be used in these exchanges.

E. Task V - Matrix Modification

1. Alumina

a. Introduction

Hydrogenation catalysts with cobalt-molybdenum and nickel-molybdenum on large pore diameter alumina supports, such as Filtrol's HPC-5 catalyst, have been shown to be active in coal liquefaction and hydrodesulfurization (12). Additional studies have been carried out on the effect of alumina support pore size distribution on the hydrodenitrogenation of heavy coal liquids (13-15). These studies all indicate the importance of support pore size distribution on catalyst activity and deactivation. Therefore, Filtrol is preparing a series of relatively large pore size alumina supports with varying pore size distributions, and good strength. Catalysts with improved ageing resistance will be produced by adding titania to the alumina (16).

b. Experimental

Relatively large pore diameter alumina supports with varying pore size distributions have been produced from Kaiser SA, and Condea SB aluminas by varying the proportion of Kaiser to Condea aluminas from 100% to 0%. In one case, titania was also added to the mixture. The physical properties of these supports and the general preparation conditions are presented in Table V.

c. Future Work

These alumina supports will be used to prepare hydrotreating catalysts (Section IV-F), and the most active aluminas will be compounded into cracking catalysts (Task VI), and hydrocracking catalysts (Task VII).

2. Synthetic Silica-Alumina, Silica-Alumina-Zirconia, and Silica-Alumina-Magnesia

The above basic matrix materials are to be prepared for further use in compounding into cracking and hydrotreating catalysts.

Over the last several weeks, a literature search has been carried out on amorphous silica-alumina, amorphous silica-magnesia, and amorphous silica-alumina-magnesia, with emphasis on their preparation and properties. The literature search covered the period 1950-1972 and included both patents and articles.

TABLE V. PHYSICAL PROPERTIES OF KAISER/CONDEA ALUMINA SUPPORTS

<u>Kaiser/Condea</u>	SA ^(a) <u>m²/g</u>	PV ^(a) <u>cc/g</u>	Pore Volume Distribution (%) ^(a)					
			----- Radius Range (Å) -----					
			<u>10-25</u>	<u>25-50</u>	<u>50-100</u>	<u>100-150</u>	<u>150-200</u>	<u>200-300</u>
100/0	224	0.84	3.3	31.2	53.8	7.8	1.8	2.0
80/20 ^(b)	197	0.73	3.0	31.6	55.6	6.6	1.7	1.5
80/20 ^(c)	196	0.66	4.9	42.0	44.1	5.9	1.6	1.4
23/77 ^(b)	202	0.69	3.5	37.4	55.5	2.4	0.6	0.6
0/100	217	0.61	8.5	46.5	44.4	0.3	0.1	0.2

(a) Measure with Micromeritics Digisorb 2500 surface area and pore volume analyzer in desorption mode.

(b) Mixed mull supports using volatile-free wt. ratios of aluminas shown. Prepared by peptizing, mulling, extruding, and calcining as 1/16" extrudates.

(c) +11 wt. % TiO₂.

Based on the collected information, a procedure has been selected to prepare silica-alumina gels from sodium silicate and sodium aluminate. The procedure is now being tested on a bench scale. Analytical data are not yet available.

We plan to prepare silica-alumina gels with different $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios. As soon as the preparation procedures are optimized, they will be used to prepare large batches of silica-alumina gel in the pilot plant.

F. Task IX - Hydrotreating Catalyst Preparation

1. Introduction

Hydrotreating catalysts are to be prepared from matrix materials such as alumina, silica-alumina, silica-alumina-zirconia, and silica-alumina-magnesia (Section IV-E). The effects of metals ratios and catalytically active components will be determined by correlating physical and chemical properties versus hydrotreating activity.

2. Experimental

Three alumina supports with Kaiser SA alumina to Condea SB (Table V) alumina ratios of 80/20, 23/77, and 80/20 + TiO_2 were produced as 1/16" extrudates as described in Section IV-E-1 of this report. The aluminas were calcined for 3 hours at 1000°F, and spray impregnated with $(\text{NH}_4)_6\text{MoO}_{24} \cdot 4\text{H}_2\text{O}$. The supports were then dried overnight at 250°F and further spray impregnated with either $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ or $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. The products were then dried at 250°F overnight and calcined at 1000°F for 3 hours. Table VI shows the proportions of MoO_3/CoO and MoO_3/NiO on the 18 catalysts prepared. Chemical analyses, surface area, pore volume, and pore size distribution measurements are pending.

3. Future Work

A second series of 18 hydrotreating catalyst will be prepared by impregnating the three Kaiser/Condea alumina supports with mixtures of WO_3/CoO and WO_3/NiO . Additional hydrotreating catalysts will be prepared from the other matrix modifications of Task V as these materials become available in pilot plant amounts.

V. CONCLUSIONS

Due to the fact that we have not received our SRC II Fuel Oil Blend, and have not begun our catalytic testing program as yet, no technical conclusions need be made at this time. However, an analysis of the work accomplished to date indicates that we may be able to make up the time lost due to the initial delays in starting the contract.

TABLE VI. METAL OXIDE CONCENTRATIONS ON ALUMINA HYDROTREATING CATALYSTS

Alumina Support Kaiser/Condea	-----Wt. % MoO ₃ /CoO-----			-----Wt. % MoO ₃ /NiO-----		
	<u>12/6</u>	<u>12/3.6</u>	<u>12/1.2</u>	<u>12/6</u>	<u>12/3.6</u>	<u>12/1.2</u>
80/20	13.25/5.96	12.96/3.71	a	12.86/5.88	12.90/3.65	a
80/20 + TiO ₂	12.75/6.38	a	a	12.36/6.39	a	a
23/77	12.92/6.28	12.39/3.82	a	12.87/6.06	12.14/3.68	a

^aAnalyses Pending

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