HYDROCRACKING WITH PILLARED CLAYS

Mario L. Occelli* and Raymond J. Rennard
Gulf Research & Development Company
P.O. Drawer 2038
Pittsburgh, PA 15230

ABSTRACT

Pillared bentonites have been prepared by ion-exchanging the clay charge compensating cations with zirconyl-aluminum halohydroxy complexes $(ZrOCl_2 \cdot Al_8(OH)_{20})^{+4}$, hydroxyaluminum oligomers $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{+7}$ and colloidal silica. These interlayered clays have 250-320 m^2/g BET surface area, 0.15-0.22 cc/g pore volume, and pore height between 6 and 9 Å; thermal stability (in air, 10 h) is limited to 550°C. After a mild thermal pretreatment at 400°C in air, their cracking activity for gas oil conversion was related to the clay cations in the following manner: Ca << (Si, Al) < (Zr,Al) < Al.

Pillared clays were evaluated for use both as a cracking component and a hydrogenation component (Ni and Mo) support for the hydrocracking of an Agha Jari vacuum gas oil (VGO) in a combined hydrodenitrogenation-hydrocracking (HDN-HC) upgrading reactor. When used as the hydrocracking component with an Al_2O_3 hydrogenation support, catalyst activity was: Ca-bentonite<(Al,Zr)-bentonite< ACH-bentonite<<HY zeolite. When used as the hydrogenation component support with 30 wt% HY zeolite as the cracking component, the activity order was Al_2O_3<<(Al,Zr)-Bentonite<(Si-Al)-Bentonite<ACH- bentonite. Pillared bentonites based hydrotreating catalysts showed superior selectivity to middle distillates.

INTRODUCTION

Bentonites pillared with oxoaluminum cations are characterized by an open, two-dimensional pore structure which behaves like a strong Lewis acid and allows sorption and transport of branched aromatics and normal paraffins.[1-3] Mesitylene diffusion in a pillared Na-bentonite is twice as fast as in Na-Y zeolite[4] and is characterized by an apparent energy of activation (6.4 kcal/mole) similar to that observed for the transport of 1,3,5-triisopropylcyclohexane in NaY. C_5-C_{10} normal paraffin equilibrium loadings resemble those observed in Mobils' ZSM-5; diffusion coefficients are, in general, significantly greater than those measured in zeolites.[3] Therefore, pillared clays could find utility as catalysts for converting high molecular weight hydrocarbons like those found in heavy oils.[5,6]

After mild steam deactivation, pillared clays exhibit cracking activity for gas oils conversion comparable to that of commercial cracking catalysts containing 15 to 25% zeolite, but they generate two to three times as much coke in the 60-80% conversion range.[5,7] Coking experiments have shown that catalytic coke may not be the main cause of catalyst deactivation during gas oil conversion. Coking

* To whom all correspondence should be addressed.

has been attributed primarily to hydrocarbon occlusion and thermal degradation within the pillared clay microspace.[8]

The following paper reports the effects of using pillared clays as cracking components or as a metals support component in composite hydrogenation-hydrocracking vacuum gas oil catalysts.

EXPERIMENTAL

Pillared Clays Preparation

Pillared clays were prepared with a bentonite sample obtained from the American Colloid Company; its chemical composition is shown in Table 1. The aluminum chloro-hydroxide (ACH) solution containing the $(Al_{13}O_4(OH)_{24}\ (HO)_{12})^{+7}$ cation and the solution containing the $(Al_8(OH)_{20}ZrO)^{+6}$ complex (RETZEL-36G) were obtained from the Reheis Chemical Company. Colloidal silica, with a SiO_2/Al_2O_3 ratio of 16, was provided by NALCO Chemicals. These solutions were added to a 20-L slurry containing 100 g of bentonite. After stirring the slurry for 1-2 h at 65°C the clay was filtered and then reslurried in 5 L of distilled water (at 65°C) to remove excess reactants. After a second filtration and wash, the clay was dryed at 120°C, crushed, and sized to <100 mesh and then used for hydrotreating catalysts preparation. X-ray diffractograms of these pillared clays are shown in Figure 1; their composition is given in Table 1.

Catalyst Forming

Two forming methods were employed. When the clay was used as the cracking component, a Harshaw Al-4100P alumina hydrate powder was calcined at 400°C and then loaded with 4% Ni-14% Mo via a one-step, co-impregnation with nickel nitrate-ammonium paramolybdate solution. The oven-dried impregnated alumina was then mix-mulled with the clay, peptized with 1% nitric acid, and extruded. The extrudates were oven-dried overnight at 120°C and then calcined at 450°C for 18 h. The composition of the finished catalysts were by weight, 70% (4 Ni-14 Mo/Al_2O_3)+ 30% clay.

When clays were used as metals support, the pillared bentonite was calcined at 400°C and then loaded with 4 Ni-14% Mo by weight using the same one-step procedure described above. The oven-dried, metals-loaded clay was then mix-mulled with ammonium Y zeolite, peptized with 1% nitric acid, and extruded. The extrudates were heat-treated as before; their composition (in wt%) were 70% (4 Ni-14 Mo/clay) + 30% HY. The ammonium Y zeolite was prepared by NH_4^+-exchanging Linde NaY until the residual sodium level was less than 0.5%.

Catalyst Testing

Pillared bentonite cracking activity was evaluated by a microactivity test similar to the one described by Ciapetta and Anderson.[9] Test conditions as well as chargestock inspections are described elsewhere.[7] Before testing, catalysts were heated (in dry air) at 400°C for 10 h. Percent conversion is defined as: $(V_f-V_p)\ 100/V_f$ where V_f is the volume of the fresh feed (FF) and V_p is the volume of product boiling above 204°C.

HDN-HC runs were conducted in an externally heated 1.43 cm ID by 122 cm stainless steel, down flow, trickle bed reactor. A 0.48 cm OD concentric thermowell running the length of the reactor was used to monitor temperatures in the reactor zones. For all runs a 75 mL catalyst bed was employed. The top 35 mL of catalyst was a commercially available Nalco NM-504 hydrotreating catalyst. The bottom 35 mL of the bed was loaded with the experimental composite hydrocracking catalyst to be evaluated. No product separation was carried out between catalyst beds. Both catalysts were sized to 16x40 mesh and presulfided in situ at 204°C and 35 psig for 6 h with 56 L/h of a 92% hydrogen-8% hydrogen sulfide gas blend.

An Agha Jari VGO containing 1500 ppm organic nitrogen and 1.2% sulfur was the feed for all runs. The reaction conditions in Table 2 were chosen to allow the hydrotreating catalyst to reduce the feed organic nitrogen and sulfur levels to <50 ppm and <0.2%, respectively; reactor configuration is shown in Figure 2. Hydrocracking test runs were 34 h in duration, with a 2-h off-stream period and five, 3 h on-stream periods at each temperature. Analyses were performed on products collected from the last on-stream period.

RESULTS AND DISCUSSION

Exchange reactions of Ca-bentonite with polynuclear cations generate molecular sieve-like materials stable to 500-600°C with 250-320 m^2/g surface area and 0.15-0.22 cc/g pore volume (Tables 1 and 3). This microspace is attributed to the pillaring induced by stable oxide clusters formed by dehydroxylating the interlayering cations. As in HY zeolites, pillared clays exhibit a narrow distribution of pore sizes with more than 85% of this area in pores with radius less than 10 Å, Table 3. At cracking conditions (400°C) in vacuo acidity in clays pillared with aluminum oxide clusters is mostly of the Lewis type; a Lewis/Bronsted (L/B) acid sites ratio of four has been found.[6] In HY, a L/B ratio of 0.6 has been estimated from literature data.[6] In powder form (100 x 325 mesh granules) pillared bentonites have (after aging in air at 400°C/10 h) cracking activity for gas oil conversion similar to that of HY (Table 4). The ranking is as follows:

Ca-Bentonite<<(Si,Al)Bentonite<(Zr,Al)Bentonite<ACH-Bentonite<HY

However, the HY zeolite retains useful cracking activity even after a hydrothermal (10 h at 730°C with 95% steam at 1 atm) aging period, whereas pillared clays do not.

To isolate the two catalysts contribution to the overall HDN-HC activity, blank runs were performed with the composite catalyst bed replaced with 37.5 mL of inert, fired quartz chips. Results in Table 5 show the ability of the commercial hydrotreating catalyst (Nalco NM-504) for sulfur and nitrogen removal. The decrease of the 360°C$^+$ fraction with temperature indicate its activity for hydrocarbon cracking; therefore, conversion over the combined HDN-HC catalyst at each temperature is expressed as,

$$CON = 100 \times (TGO^B - TGO^R)/TGO^B,$$

where TGO^B and TGO^R are the 360°C$^+$ content of the blank and run product, respectively.

Three clays (Ca-bentonite, ACH-bentonite, and (Al,Zr) bentonite) were tested, along with HY, as cracking components in composite catalysts containing 70% alumina loaded with 14% Mo and 4% Ni. Results in Table 6 show that bentonite pillared with Al_2O_3-clusters (ACH-bentonite) is the most active clay for VGO cracking; at 400°C it is significantly less active than the HY-containing catalyst. While the relative ranking of the catalysts in terms of activity is the same as that observed in cracking gas oils, the hydrocracking activity differences between pillared clays and HY zeolite are much more pronounced. At 415°C this difference is even more evident (see Table 6). In fact, while the activity of the zeolite-containing catalyst increases to 98.3% (up from 48.2% at 400°C), the activity of the ACH-bentonite containing catalyst remained unchanged at 31-32%. Rapid deactivation due to hydrocarbons occlusion and coking, is believed responsible for the pillared clays apparent low hydrocracking activity (see Table 6).

ACH-bentonite (Si,Al)-Bentonite and (Al,Zr)-Bentonite were used as metal (14% Mo + 4% Ni) support in composite catalysts promoted with 30% HY for hydrocracking activity. A similar catalyst containing metal-loaded alumina (and 30% HY) was used as reference material. Results in Table 7 indicate the greater activity of the pillared clays containing catalysts and their selectivity with respect to light furnace oil (LFO) generation. The rapid deactivation previously observed was not evident in these runs. Metal loading the pillared clays may have reduced their acidity and minimized coke formation. (Al,Zr) pillared bentonite has greater cracking activity than (Si,Al) bentonite (Table 4). The higher hydrocracking activity of the (Si,Al) bentonite composite catalyst with respect to the one containing (Zr,Al) Bentonite (see Table 7) is due to the different surface area of these pillared clays (Table 3). As expected, the ACH-bentonite containing catalyst was most active. At 400°C conversion was 70% and generated a liquid containing 37.7% LFO. The selectivity of these clays for LFO production during VGO hydrocracking can be attributed to the pillared clay microporous structure, which appears to control the cleavage of high molecular weight hydrocarbons and retards further cracking to lighter fractions.

CONCLUSION

Because of rapid deactivation due to excessive coke formation, pillared clays are ineffective when used as the cracking component in composite hydrocracking catalysts. When used as metals supports in composite catalysts containing zeolites, the pillared clays show excellent hydrocracking activity and selectivity to light furnace oil. This is probably due to the moderation of their acidity resulting from the addition of hydrogenation metals like Mo and Ni and to the open microstructure resulting from pillaring.

REFERENCES

1. D. E. W. Vaughan and R. J. Lussier, "Preparation of Molecular Sieves Based on Pillared Interlayered Clays (PILC)," Proc. 5th Inter. Conf. Zeolites," L. V. Rees, Ed., Heyden, London 1980, 94.

2. M. L. Occelli, and R. M. Tindwa, "Physicochemical Properties of Montmorillonite Interlayered with Cationic Oxyaluminum Pillars," Clays and Clay Minerals 1983, 31, 1, 22.

3. M. L. Occelli, V. Parulekar, and J. W. Hightower, Proc. 8th Inter. Congress Catalysis, Berlin (1984), in press.

4. M. L. Occelli, R. A. Innes, F. S. S. Hwu, and J. W. Hightower, "Catalytic Activity of Sodium-Montmorillonite Interlayered with Aluminum Oxide Clusters," J. Applied Catalysis 1984, Submitted.

5. D. E. W. Vaughan, R. J. Lussier, and J. S. Magee (1970), U.S. Patent No. 4, 175,090.

6. D. E. W. Vaughan, R. J. Lussier, and J. S. Magee (1981), U.S. Patent No. 4, 248,739.

7. M. L. Occelli, I&EC Prod. Res. Dev. Journal 1983, 22, 4 (1983), p. 553.

8. M. L. Occelli and J. E. Lester, I&EC Prod. Res. Dev. Journal (1984), Submitted.

9. F. G. Ciapetta and D. Anderson, Oil and Gas J., 65 (1967), 88.

FIGURE 1:

X-RAY DIFFRACTOGRAMS OF (a) BENTONITE BEFORE AND AFTER PILLARING WITH (b) Al (c) Al AND Zr (d) Al AND Si OXIDE CLUSTERS. CLAYS WERE HEATED FOR 10H AT 300°C IN AIR

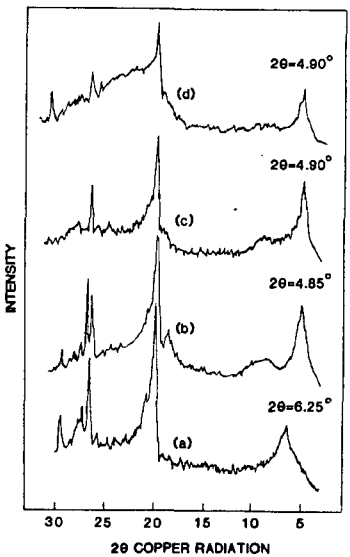

Figure 2

HDN-HC REACTOR CONFIGURATION

```
                                          ||    | FLOW
                                          ||    v
 o                                       /  \
T C          = 380-415                  |____|
LHSV         =   1.0                    |XXXX|
PSIG         = 2000                     |XXXX|
H , scf/bbl  = 6000                     |XXXX|
 2                                      |XXXX|
                                        |XXXX| <---- 37.5 ML NM-504
FEED         = AGHA JARI VGO            |XXXX|
S, wt%       = 1.75                     |XXXX|
N, ppm       = 1500                     |XXXX|
o                                       |XXXX|
 API         = 23.1                     |----|
                                        |----|
                                        |////|
                                        |////|
                                        |////|
                                        |////|
                                        |////| <---- 37.5 ML COMPOSITE
                                        |////|
                                        |////|
                                        |////|
                                        |////|
                                        |____|
                                        |    |
                                         \  /
                                          ||
                                          ||
```

Table 1. Bentonite composition before and after pillaring (Galbraith Laboratories Data).

	Oxides Composition (Wt%)			
	Calcium Bentonite	ACH-Bentonite	(Zr-Al) Bentonite	(Si-Al) Bentonite
SiO_2	62.9	55.9	55.3	78.1
Al_2O_3	20.0	31.6	25.8	13.9
Na_2O	0.53	0.67	0.50	0.35
K_2O	2.32	0.37	0.35	0.20
MgO	2.16	1.55	1.58	0.90
CaO	2.58	0.43	0.24	0.48
Fe_2O_3	4.38	3.59	3.60	1.8
ZrO_2	--	-	6.1	--

Table 2. Hydrotreating-hydrocracking run conditions.

Feedstock	Agha Jari VGO
Gravity, °API	23.1
Sulfur, wt%	1.75
Nitrogen, ppm	1500
Temperature, °C	390-415
Pressure, kpa (psig)	13,891 (2000)
Catalyst Volume, mL	37.5 Hydrotreating 37.5 Hydrocracking
Catalyst Bed Length, cm	52.8
LHVS, h^{-1}	1.0
Feed Volume, mL/h	75
Hydrogen/Oil, m^3/m^3 (scf/bbl)	1069 (6000)

Table 3. Pillared clays surface properties after heating in dry air at 400°C/10 h and sizing to 100x325 mesh granules.

	ACH-Bentonite	(Zr,Al) Bentonite	(Si,Al) Bentonite	Calcium Bentonite	HY Linde
BET Surface Area (m^2/g)	255.0	254.0	303.5	46.6	508
Pore volume (cc/g)	0.16	0.17	0.21	0.08	0.32
Pore Volume Distribution					
Area % in Pores with Radius					
< 10 Å	88.0	90.0	87.8	25.2	94.9
10 < R <20 Å	9.4	7.1	8.6	36.1	2.3
20 < R <100 Å	2.4	2.4	3.2	29.1	1.4
> 100 Å	0.2	0.5	0.4	9.6	1.4

Table 4. Cracking activity for gas oil conversion before and after pillaring. Clays were heated at 400°C/10 h in dry air and sized to 100 x 325 mesh before testing.

	Calcium Bentonite	ACH-Bentonite	(Zr,Al) Bentonite	(Si,Al) Bentonite
Conversion (V% ff)	28.4	82.1	73.8	67.9
Gasoline (V% ff)	16.7	59.8	55.6	51.5
Furnace Oil (V% ff)	30.3	13.6	19.0	22.3
Slurry Oil (V% ff)	41.6	4.2	7.2	9.8
Hydrogen (wt% ff)	0.75	0.24	0.21	0.28
Carbon (wt% ff)	7.8	12.2	9.6	7.48

Table 5. HDN-HC blank runs.

Component	T°C	% NAP	% KER	% LFO	% TGO	°API	% CON	% S	ppm N
Quartz	380	0.9	3.5	15.6	83.4	28.3	0	0.0	50
Quartz	390	1.6	3.9	16.9	81.5	32.3	0	0.0	30
Quartz	400	3.3	7.8	24.1	72.6	31.2	0	0.0	<20
Quartz	415	6.6	13.5	32.2	61.2	33.3	0	0.0	<10

Table 6. HDC-HC with pillared clays as cracking component.

Cracking Component	Reactor T°C	Liquid Composition* % NAP	% KER	% LFO	% TGO	°API	% CON
HY Zeolite	400	28.0	29.5	34.4	37.6	41.3	48.2
	415	80.0	34.1	18.1	1.0	54.1	98.3
ACH-Bentonite	400	11.6	21.9	39.0	49.5	36.5	31.8
	415	14.2	26.8	43.9	41.9	37.9	31.5
(Al,Zr) Bentonite	400	9.2	14.9	31.2	59.7	34.6	17.8
	415	11.8	19.0	36.6	51.7	36.2	15.5
Ca-Bentonite	400	6.6	14.3	32.7	60.6	34.4	16.5
	415	11.6	21.7	41.4	47.0	36.6	23.2

NAP = Naptha (OP-154°C)
KER = Kerosene (190-271°C)
LFO = Light Furnace Oil (190-360°C)
TGO = Total Gas Oil (360°C+)

Table 7. HDN-HC with clays as hydrogenation component support at 400°C.

Support	Reactor T°C	Liquid Composition* % NAP	% KER	% LFO	% TGO	°API	% CON
Alumina	390	13.1	17.5	28.4	58.6	35.4	28.1
	400	28.0	29.5	34.4	37.6	41.3	48.2
(Al,Zr) Bentonite	390	14.6	25.2	34.6	50.8	36.0	37.7
	400	27.2	32.0	36.4	36.4	40.5	49.9
(Si-Al) Bentonite	390	21.4	26.9	36.7	41.9	39.5	48.6
	400	34.5	30.5	35.8	39.6	42.9	59.2
ACH-Bentonite	390	20.3	34.6	43.4	36.3	40.5	55.5
	400	40.6	35.7	37.7	21.7	45.0	70.1

(a) NAP = Naphtha (OP-154°C); (b) KER = Kerosene (190-271°C); (c) LFO = Light Furnace Oil (190-360°C); (d) TGO = Total Gas Oil (360°C+).

Table 8. HDN-HC with clays as hydrogenation component support at 390°C.

Component	T°C	% NAP	% KER	% LFO	% TGO	°API	% CON
Alumina	390	13.1	17.5	28.4	58.6	35.4	28.1
ACH-Bentonite	390	20.3	34.6	43.4	36.3	40.5	55.5
Si-Bentonite	390	21.4	26.9	36.7	41.9	39.5	48.6
Al,Zr-Bentonite	390	14.6	25.2	34.6	50.8	36.5	37.7

(a) NAP = Naphtha (OP-154°C); (b) KER = Kerosene (190-271°C); (c) LFO = Light Furnace Oil (190-360°C); (d) TGO = Total Gas Oil (360°C+).