Part II

PHYSICAL PROPERTIES
EVALUATION OF COMPOUNDS AND MATERIALS

Stability of Hydrocracking Catalysts

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PRODUCT VALUE declines in many hydrocracking applications during on-stream operation because of increased dry gas make, decreased liquid yield, and a shift toward less valuable products boiling below reformer charge (180° to 390° F.). Catalyst activity also declines. To realize a practical catalyst life, either this decline must be held to a tolerable rate—e.g., by using high hydrogen partial pressure—or the catalyst must be periodically regenerated. Periodic regeneration seemed more practical; therefore, performance of catalysts was compared in repeated cycles of gas oil hydrocracking and regeneration.

The catalysts all have acidic sites and hydrogenation-dehydrogenation sites (*2–6*, *9*). The acid sites isomerize and crack olefin intermediates made at the hydrogenation sites, the products being converted to saturates at the hydrogenation-dehydrogenation sites (*2*, *5*).

EXPERIMENTAL

Materials. Several large batches of a straight-run heavy Mid-Continent distillate gas oil were used. Average properties were: B.P., initial, 615° F.; 5 volume %, 680° F.; 50%, 785° F.; 95%, 935° F. Density 0.896 gram/cc. at 15° C.; aniline number, 189; N, 0.07 weight %; S, 0.55 weight %, O, 0.45 weight %. In one experiment, a corresponding Mid-Continent light gas oil was used; pertinent properties are a nominal boiling range of 400° to 650° F., and 0.5 weight % O.

Cyclohexane was Phillips pure grade (99+ %), benzene was Eastman thiophene free grade (melting range, 5–5.5° C.), *n*-hexadecane was Humphrey-Wilkinson ASTM grade, methanol was Baker absolute grade (99.9+ %), furan was Eastman (boiling range, 31–32° C.), thiophene was Eastman (boiling range, 83 to 85° C.), and pyridine was Eastman (boiling range, 113.5 to 115.5° C.).

Hydrogen was passed through Deoxo cylinders (palladium catalyst) to convert traces of oxygen to water, dried over Mobil Sorbead (desiccant silica-alumina), and passed over activated charcoal to remove traces of oil introduced during compression. Cyclohexane and *n*-hexadecane were percolated through silica gel before use. All other materials were used without special purification.

Catalyst compositions are listed in Table I.

Procedures. Three hydrocarbon conversion reactions were used: the main reaction of hydrocracking and two indicator reactions, cyclohexane dehydrogenation to benzene and the reverse. Reaction conditions for each are listed in Table II. Processing was bench scale (5.5 mg. of catalyst for cyclohexane dehydrogenation, 100 to 300 cc. of catalyst in the other cases) without either liquid or gas recycle. Product analysis depended on mass spectrometry, gas chromatography, and analytical distillation used alone or in combinations. Surface areas were determined by a modified Brunauer-Emmett-Teller procedure using nitrogen at −195° C.

Coked catalysts were regenerated with 2% oxygen in nitrogen, starting at 750° F. and finishing at 900° F. with platinum catalysts. For all other catalysts, cleanup was with air at 1000° F. Sulfide-type catalysts were resulfided after each regeneration with 50% hydrogen sulfide in hydrogen at 800° F. Catalysts were regenerated at least four times between periods of gas oil hydrocracking lasting 6, 3, 3, 3, and 6 days. In some cases, more regenerations were practiced.

Under the conditions used, all catalysts aged (lost activity) during heavy gas oil processing, and this aging was compensated for by continually increasing reactor temperature. Within narrow temperature ranges, constant density of liquid product during hydrocracking corresponds roughly to constant conversion, 0.792 gram per ml. at 15° C.

Table I. Catalysts

Catalyst No.	Surface Area, Sq. M./G.	Support Compn., Wt. %			Added Components, Wt. % on Support						
		SiO_2	Al_2O_3	ZrO_2	Pt	Ni	W	CoO	MoO_3	Cl	S
1	615	90	...	10	0.51	...	...	...	...	0.20	...
2	535[a]	90	...	10	0.50	...	...	...	...	0.19	...
3	395	90	10	...	0.46	...	...	...	...	0.02	...
4	380	90	...	10	0.51	...	...	...	...	0.12	...
5	360	75	...	25	0.53	...	...	...	...	0.55	...
6	325	75	25	...	0.50	...	...	...	...	...	...
7	285	75	25	...	0.50	...	...	...	...	0.02	...
8	220	90	10	...	0.48	...	...	...	...	0.02	...
9	235	90	10	...	...	4.5	10	...	...	...	5.5
10	430[a]	90	...	10	...	...	...	3.0	11.1	...	5.5
11	220	15	85	...	...	...	...	2.5	8.5	...	3.7
12	460[a]	90	...	10	...	...	...	...	9.1	...	3.3

[a] Catalysts made with SiO_a-ZrO_2 of 615 ± 15 sq. m./g.

Table II. Reaction Conditions

	Pressure, P.S.I.G.	Space Velocity, Liquid Vol./Hr. Vol. Catalyst	Molar Ratio, H_2 to Hydrocarbon	Temp., ° F.	Conversion Level, %
Hydrocracking	2000	0.5	9.5	780–850[a]	70–85
Cyclohexane dehydrogenation[b]	350	20,000[c]	4.0	750	0–7
Benzene hydrogenation	1000	2.0	10.0	700	10–100

[a] Temp. adjusted to give 0.792-g./cc. liquid product (at 15° C.) from Mid-Continent heavy gas oil. [b] Relative DA test.

[c] Approx., precise conditions are 5.5 mg. of catalyst and 100 cc. of cyclohexane/hr.

corresponding to 40% conversion of the heavy gas oil to products boiling below 390° F., and to 80% conversion to products boiling below 650° F. Reactor temperature was continually adjusted to give this product density. Activity is defined as the temperature giving this product density after 48 hours on stream. Aging rate is the daily increase in temperature required to maintain that product density thereafter. In the catalyst comparisons, variations in the actual conversions as determined by product analysis are compensated for by adjusting all results to a common basis, 40% conversion to products boiling below 390° F. In the cases of catalysts 2, 3, and 11, this was done by by interpolating between results of experiments in which conversion was deliberately varied over a range of about 10%. In all other cases, the rate of change of yield of each product fraction with conversion was assumed to be the same as that of catalyst 2 (for platinum and nickel-tungsten-sulfide catalysts) and of catalyst 11 (for cobalt-molybdena catalysts).

The light gas oil, *n*-hexadecane, and blends of oxygen, nitrogen, or sulfur compounds in *n*-hexadecane were also hydrocracked at the conditions of Table II, except for conversion levels. The catalyst in these experiments was catalyst 2, and the temperature schedule matched that of heavy gas oil hydrocracking over that catalyst.

Relative DA Test. The dehydrogenation-activity test was modified in our laboratories by L.C. Drake, C.J. Plank, and R.B. Smith from a cyclohexane dehydrogenation test described earlier (7). The conditions (Table II) give benzene yields well below that at equilibrium. Benzene yield over a given catalyst is reported as a percentage of the benzene yield over Engelhard Industries RD-150.6 platinum reforming catalyst in the same test. The yield over RD-150.6 catalyst varied somewhat between standardization runs. Therefore the yield over RD-150.6 catalyst used in calculating relative DA is taken as the average from preceding and following standardization runs.

Benzene Hydrogenation Test. This test was developed in our laboratories by S.C. Eastwood, R.J. Kelly, and S.J. Wantuck to indicate hydrogenation-dehydrogenation activities of low DA catalysts. Contact time is much greater than in the relative DA test and 1% thiophene is added to the benzene when testing sulfide-type catalysts; other details are given in Table II. In this test, the fresh platinum catalysts all gave complete hydrogenation of the benzene.

Direct Steaming Experiments. Catalyst samples (5 cc.) were steamed in cylindrical 50-mesh stainless steel baskets suspended in a 5-gallon autoclave. Up to 13 catalysts were treated simultaneously. All connecting lines in which steam might have condensed were wrapped with heating tape and maintained hot enough to prevent condensation. Steam partial pressures were determined with a cold gage which was initially filled with hydrogen to a pressure a little greater than that expected at reaction temperature from vaporization of the water added to the autoclave. This gage was closed off from the autoclave until reaction temperature was reached.

To standardize all catalysts as to initial moisture content, catalyst samples were calcined in air at 800° F. for 16 hours before being placed in the autoclave. The autoclave was then evacuated to a pressure below 1 mm. of mercury and slowly heated to reaction temperature. (These pretreatment steps had no effect on the surface area of any catalyst.) When the autoclave was at temperature, water was forced in through a valve from a buret by 15 p.s.i.g. of nitrogen pressure. Steam partial pressure was then read by opening the valve to the gage which had been prepressured with hydrogen gas, after which that gage was again closed off from the system. When hydrogen or nitrogen partial pressure was used with steam partial pressure, the fixed gases were added last.

At the end of a steaming period, gases were vented to traps at −80° C., and then the autoclave was evacuated through those traps during cooling. Thus, the steam acted on the catalysts only during a well defined time interval.

Hydrogen at 3200 p.s.i.g. and/or nitrogen at 2000 p.s.i.g. were passed through a Deoxo unit and then a 4-A Linde Molecular Sieve drier before being fed to the autoclave.

Analysis for Oxygen Content of Gas Oils. Combined oxygen content in gas oils was determined by a modified Unterzaucher method. The gas oil sample was pyrolyzed in a stream of flowing nitrogen. Gaseous pyrolysis products were first passed over carbon at 1120° C., where oxygen derived from decomposition of the sample was converted to carbon monoxide; then passed over copper oxide at 350° C. where carbon monoxide was converted to carbon dioxide; and finally, through 8- to 20-mesh Ascarite (sodium hydroxide on asbestos) mixed with Anhydrone (magnesium perchlorate). The Ascarite reacts with the carbon dioxide to form sodium carbonate and water, and the Anhydrone takes up the water. Thus, the increase in weight in Ascarite-Anhydrone tube measures the carbon dioxide equivalent to the oxygen content of the gas oil. A blank determination with nothing in the platinum sample boat is made before each analysis, and the result, which is almost constant at 40-μg. increase in weight, is subtracted from the result with the sample in the boat. Sample size is 40 mg. at 1.0 weight % oxygen in the sample; duplicability is 0.18 weight % based on 29 repeated determinations.

FRESH CATALYST PERFORMANCE

With the heavy gas oil of these experiments, desirable catalyst performance in hydrocracking gives high yields of C_5+ products and or heavy naphtha (reformer feed boiling from 170° to 390° F.), low make of dry gas (C_1 to C_3 hydrocarbons), high activity (low temperature for a given conversion), and low aging rate. Catalyst selectivity refers to the above product distribution characteristics considered together—with heaviest emphasis on C_5+ and heavy naphtha yields.

Fresh catalyst performances during the third day on stream are reported in order of decreasing selectivity in Table III. They indicate that platinum and nickel-tungsten sulfide catalysts are often more selective than cobalt oxide–molybdena-sulfide catalysts, and that high selectivity and activity often go together. They suggest that neither high dehydrogenation activity—as measured by relative DA—nor very high surface area are needed for either high selectivity or activity. In spite of immeasurably low DA and relatively low surface area, the nickel tungsten sulfide catalyst was both active and selective.

The benzene hydrogenation test is particularly adapted to measuring the hydrogenation-dehydrogenation activities of low DA catalysts. Using this test, three of the four nonplatinum catalysts are compared with a platinum catalyst (No. 2) in Table IV. Fresh catalyst results from this comparison line up as follows:

Catalyst		% Benzene Hydrogenated
No.	Description	
2	Pt on 90/10 Si/Zr	100
9	Ni/W/S on 90/10 Si/Al	43
11	Co/MO/S on 15/85 Si/Al	22
10	Co/Mo/S on 90/10 Si/Zr	17

Of these, the top two have high and approximately equal hydrocracking selectivities, and the bottom two have low and approximately equal selectivities. These results conform with the generality of Coonradt and others (*4*) that high selectivity requires some minimum of hydrogenation-dehydrogenation activity. That minimum appears from Table IV to lie above that of the cobalt-molybdena catalysts (20% benzene hydrogenated) and below that of the nickel-tungsten catalyst (43% benzene hydrogenated). Together, the data of Tables III and IV fit idea that catalyst hydrogenation-dehydrogenation sites were rate-controlling initially with the cobalt-molybdena catalysts, whereas acid sites were rate-controlling with the platinum and nickel-tungsten-sulfide catalysts.

STABILITY DURING HYDROCRACKING-REGENERATION CYCLES

Catalysts were regenerated four times between periods of gas oil hydrocracking lasting 6, 3, 3, 3, and 6 days. Results are reported in Table V as the average change in each performance characteristic per cycle of hydrocracking and regeneration. (Hydrocracking results are from the third day on stream in the beginning and after the last regeneration.) Just as in initial performance, the catalysts are not lined up in the same way for each performance characteristic. In Table V, equal and heaviest emphasis was placed on stability of C_5+ and heavy naphtha yields.

Table III. Platinum and Nickel–Tungsten–Sulfide Catalyst Were Generally More Selective Initially

				Indices of Hydrocracking Performance[a]				
				Primary[b]		Secondary[b]		
No.	Catalyst Description	Surface Area, Sq. M./G.	Relative DA[c]	C_5+ yield, vol. %	Heavy naphtha, vol. %[d]	Dry gas wt. %	Activity, ° F., for ca. 40% conversion[e]	Aging rate ° F./day
6	Pt on 75/25 Si/Al	325	90	108.5	38.5	2.1	780	2
2	Pt on 90/10 Si/Zr[f]	535	95	107.5	37	2.4	790	2.5
4	Pt on 90/10 Si/Zr	380	40	107.5	37	2.4	800	2.5
9	Ni/W/S on 90/10 Si/Al	235	0	107.5	36.5	3.0	780	2.5
3	Pt on 90/10 Si/Al	395	110	107.5	36	2.3	805	3.5
7	Pt on 75/25 Si/Al	285	130	107	37	2.4	775	2
8	Pt on 90/10 Si/Al	220	135	107	36	2.7	830	4
5	Pt on 75/25 Si/Zr	360	...	106.5	34	2.4	780	2
12	Mo/S on 90/10 Si/Zr	460	0	106	35.5	3.0	800	5
10	Co/Mo/S on 90/10 Si/Zr	430	0	105.5	34	3.6	800	3.5
11	Co/Mo/S on 15/85 Si/Al	220	0	104	34.5	4.7	840	3.5
1	Pt on 90/10 Si/Zr	615	45	105	32	2.9	800	...

[a] At 2000 p.s.i.g., 0.5 vol. charge/hr./vol. catalyst, 3000 SCF of H_2 charge/bbl. gas oil charge, 40% conversion of heavy Mid-Continent gas oil to products boiling below 390° F., 2-3 day material balance. [b] Repeatabilities, including repeatability of catalyst preparation, are: ±1 vol. % in C_5+ and/or heavy naphtha yield, ±0.4 wt. % in dry gas yield, ±7° F. in activity, ±1° F./day in aging rate, ±15 in relative DA. [c] Rate of cyclohexane dehydrogenation to benzene relative to that of RD-150.6 reforming catalyst. [d] Reformer charge, 180° to 390° F. [e] Temperature required to produce 0.792 g./cc. (15° C.) liquid product at 48 hr. on stream. [f] Results are averages from 8 determinations; all other results in tables are from single determinations.

Table IV. Platinum and Nickel-Tungsten-Sulfide Catalysts Were Highest in Benzene Hydrogenation Activity

	Fresh Catalyst			Regenerated Catalyst[a]			
		Mole % Yield of Hydrogenated Products				Mole % Yield of Hydrogenated Products	
No.[b]	% Benzene Hydrogenated[c]	Cyclics	Paraffins	Regeneration No.	% Benzene Hydrogenated[c]	Cyclics	Paraffins
2	100	...	...	9	75	66	11
9	43	32	14	7	35	24	14
11	22	11	13	9	21	10	13
10	17	7	11	9	11	4	8

[a] After indicated number of regenerations between periods of hydrocracking lasting 6, 3, 3, 3, 10,10, 10, 10, and 3 days, respectively. See footnote [b], Table III for hydrocracking and regeneration conditions. [b] Description in Table III. [c] 1000 p.s.i.g., 2 vol. C_6H_6/hr./vol. catalysts, 10 mole H_2/mole C_6H_6, 700° F., 1% thiophene added to benzene charge with catalysts 9, 10, and 11.

Table V. Cobalt-Molybdena Catalysts Were More Stable

		Changes per Hydrocracking-Regeneration Cycle[a]					Final	
No.	Catalyst[b], Sq. M./G.	C_5+ yield, vol. %	Heavy naphtha, vol. %	Dry gas, wt. %	Activity, ° F., for ca. 40% conversion	Aging rate, ° F./day	Relative DA[c]	Surface area, sq. m./g.
11	220	0.0	0.0	0.00	+2.5	−0.1	0	160
10	430	−0.2	0.0	0.00	+3.5	0.0	0	330
12	460	−0.1	−0.3	+0.1	+6	−0.1	0	355
9	235	−0.5	−0.4	+0.05	+5.5	+0.1	0	130
2	540	−0.4	−0.9	+0.1	+3	+0.2	30	395
6	325	−0.7	−1.3	+0.25	+4	+0.1	50	215
5	360	−1.0	−1.4	+0.55	+14.5	+6	5	255
7	285	−1.1	−2.0	+0.4	+6	+1.1	0	145
8	220	−1.1	−1.9	+0.45	+6.5	+0.9	30	165
3	395	−1.3	−1.7	+0.45	+11	+1.0	20	235
4	380	−1.2	−2.0	+0.35	+6	+1.3	0	260

[a] Four regenerations with 2% O_2 between periods of hydrocracking lasting 6, 3, 3, 3, and 10 days, respectively. See footnote [a], Table III and text for hydrocracking and regeneration conditions and other details. [b] Description in Table III. [c] Rate of cyclohexane dehydrogenation to benzene relative to that of RD-150.6 reforming catalyst.

Table VI. Surface Area, Hydrogenation-Dehydrogenation Activity, and Hydrocracking Performance Fall off with Increasing Cycle Number

(Catalyst 2)

			Hydrocracking Performance[a]			
After Cycle No.	Surface Area, Sq. M./G.	Relative DA[b]	C_5+ yield vol. %	Heavy naphtha, vol. %	Dry gas, wt. %	Activity, ° F. for 0.792 g./cc. product at 48 hr.
Fresh[c]	540	110	108.5	38.5	2.0	795
1	465	65	107.5	34.5	2.3	810
2	430	45	106.5	34.5	2.7	805
3	450	30	106.5	33.5	2.7	810
4	395	30	107	35	2.3	805
5	390	...	105.5	33	2.9	805
6	410	30	103.5	31	3.4	825
7	370	15	102.5	29.5	3.8	825

[a] Conditions of footnote [a], Table III. [b] Rate of cyclohexane dehydrogenation to benzene relative to that of RD-150.6 reforming catalyst. [c] For one test of a single preparation of catalyst.

The results clearly indicate the superior stability of molybdena and cobalt-molybdena catalysts, the generally lesser stability of platinum catalysts, and the intermediate position of the nickel-tungsten-sulfide catalyst. They indicate that when regenerations are frequent, cobalt-molybdena catalysts seem the better choice.

The losses in hydrocracking performance characteristics are expressed as average losses per cycle in Table V. In actual fact, the rate of loss is lower in the initial cycles and increases with increasing number of cycles. This is shown in detail for catalyst 2 in Figure 1. Moreover, the rate of decline in selectivity during on-stream hydrocracking increases within each cycle as a function of stream time. Therefore, in actual practice, on-stream time will be shorter with each succeeding regeneration.

STABILITY FACTORS

For all of the catalysts, hydrogenation-dehydrogenation activity and surface area fall off during hydrocracking-regeneration cycles. For catalyst 2, these losses correlate with each other and with the losses in hydrocracking performance (Table VI). These correlations, however, may not reflect the actual mechanisms underlying the observed deterioration in hydrocracking performance. If the catalyst has enough hydrogenation-dehydrogenation activity left to make the acid sites rate controlling during the last hydrocracking-regeneration cycle, the drop in catalyst DA during the cycles cannot be the reason for the deteriorating hydrocracking performance. This is definitely possible. The lack of DA of the active and selective nickel-tungsten catalyst (Table III) shows that the correlation between DA

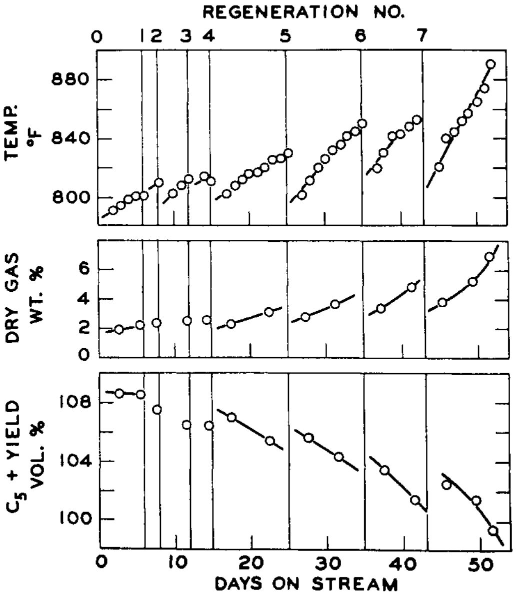

Figure 1. Catalyst 2 under standard conditions gives a typical example of declining catalyst performance in hydrocracking-regeneration cycles

and hydrocracking performance in Table VI cannot be literally meaningful. It would have to be assumed that the effective hydrogenation-dehydrogenation activities (during actual hydrocracking in the third day on stream, when selectivities were determined) were lower than and correlated with the DA values measured before hydrocracking was started.

More platinum was added by chloroplatinic acid impregnation to catalyst 3, platinum on 46-AI silica-alumina (*1*), after the fifth hydrocracking-regeneration cycle. This brought the platinum content up from 0.5 weight % to 1.0 weight %, and the relative DA up from 20 to 90. However, hydrocracking activity or selectivity did not change.

With acid site rate-controlling in the cyclic test, on the other hand, loss in surface area of the support contributing the acidity might be expected to correlate with deteriorating hydrocracking performance. Such a correlation exists with the platinum catalyst of Table VI, but not with the cobalt-molybdena catalysts. They lost 35 to 40% of their original surface areas with little or no loss in hydrocracking performance (cf. Tables III and V). The results are reasonable if the platinum catalyst had more hydrogenation-dehydrogenation activity than necessary for high selectivity after each regeneration of the cyclic test, whereas the cobalt-molybdena catalysts did not. Then acidity was rate controlling with the platinum catalyst; its decline caused deteriorating hydrocracking performance; and surface area loss might index the loss in acidity. For the cobalt-molybdena catalysts, on the other hand, hydrogenation-dehydrogenation activity would be rate-controlling; neither loss in surface area nor acidity would be reflected in catalyst performance. The relative stability of catalyst performance would come from stability of the hydrogenation-dehydrogenation component.

Consequently, hydrocracking performance would not be expected to correlate with either DA or benzene hydrogenation activities above about 20% benzene hydrogenated, but would be expected to correlate with benzene hydrogenation activities below that level. Our available data are not enough to substantiate the idea.

CAUSE OF SURFACE AREA LOSS

Loss in catalyst surface area during a single cycle of hydrocracking and regeneration correlates with the partial pressure of water derivable from chemically combined oxygen in the charge—whether this oxygen is naturally occurring or artificially added (Table VII). The loss does not correlate with the amount of coke made during hydrocracking and subsequently burned off during regeneration, with the structures of hydrocarbon charge components or of oxygenated compounds used to dope the hydrocarbon charge, or with the amount of combined nitrogen (as pyridine) or combined sulfur (as thiophene) in the charge. These results fit the conclusion that water—made by hydrocracking oxygen compounds in the charge rather than by coke burning in the regenerator—steams down catalyst surface area.

DIRECT STEAMING OF CATALYSTS

Table VII shows results from hydrocracking experiments lasting 6 days at 780° to 800° F. Tables VIII and IX present the results of treating fresh catalysts with directly added steam in an autoclave. Table VIII shows that neither 2000 p.s.i.g. of hydrogen nor nitrogen causes the catalyst to lose surface area at conditions under which 35 p.s.i.a. of steam does. Moreover, adding hydrogen

Table VII. Water Made during On-Stream Hydrocracking Steams Down Surface Area

(Catalyst 2)

Charge to Hydrocracking	O Concn. in charge, Wt. %	Hydrocracking Press., P.S.I.G.[a]	Max. Part. Press. of Steam, P.S.I.A.	Coke on Catalyst as C, Wt. %	Loss in Surface Area, %
n-Hexadecane + 1.2% O as furan	1.3	2000	47.5	0.4	23
n-Hexadecane + 1.0% O as furan	1.1	2000	40	0.2	24
n-Hexadecane + 1.0% O as furan	1.1	2000	40	0.4	22
Mid-Continent Heavy gas oil, 650°-950° F.	0.75	2000	32.5	4.8	22
Mid-Continent Light gas oil, 400°-650° F.	0.5	2000	20.5	0.3	10
n-Hexadecane + 1.0% O as furan	1.1	1000	20.5	0.5	12
Mid-Continent Heavy gas oil, 650°-950° F.	0.45	2000	19.5	3.9	13
Mid-Continent Heavy gas oil, 650°-950° F.	0.45	2000	19	2.5	16
n-Hexadecane + 0.4% O as furan	0.5	2000	18.5	0.7	12
n-Hexadecane + 1.0% O as furan	1.1	500	10.5	3.7	5
Unpercolated *n*-hexadecane	0.2	2000	6	0.3	3
n-Hexadecane + 1.0% N as pyridine	0.2	2000	6	0.3	7
n-Hexadecane + 1.0% S as thiophene	0.1	2000	3.5	0.3	4
n-Hexadecane	0.1	2000	3.5	0.3	2

[a] Other conditions: 9.5 mole H_2/mole of heavy gas oil; 0.5 vol. hydrocarbon/hr./vol. catalyst; start at 680° F., raise to 780° F. in 6 hr., raise 3° F./day thereafter, total on-stream time of 6 days. Temperature schedule (gives constant product gravity of 0.792 g./cc. with heavy gas oil.) Catalyst was then regenerated before surface area was measured.

Table VIII. Surface Area Loss by Steaming Is Unaffected by Hydrogen Partial Pressure

	N_2, p.s.i.g.	. . .	1950	. . .	. . .	. . .	. . .	. . .
	H_2, p.s.i.g.	. . .	. . .	2000	. . .	2150	. . .	1800
	H_2O, p.s.i.a.	. . .	. . .	. . .	37.5	36	36.5	33.5
	Time, days[a]	. . .	2	2	2	2	1	1
Catalyst No.	Catalyst Description	Surface Area, Sq. M/G.						
	90/10 Si/Zr	610[b]	610	610[c]	490	480	540	515
2	Pt on 90/10 Si/Zr[d]	550[c]	535	520[c]	430	430	475	480
	90/10 Si/Al	405	410	405	265	275	335	315
3	Pt on 90/10 Si/Al[d]	380	375	370	250	260	300	285

[a] 800° F. [b] ±5. [c] ±10. [d] Duplicate preparation of catalyst in Table I.

Table IX. Loss in Area Is Rapid at First, but Soon Slows Down

(Steaming at 800° F. with 35 ±2.5 P.S.I.A. of water)

	Time, hours	0	4	24	48	240
Catalyst No.	Catalyst Description	Surface Area, Sq. M./G.				
	90/10 Si/Zr	610[a]	560	540	490	450
2	Pt on 90/10 Si/Zr[b]	550[c]	490	475	430	420
10	Co/Mo on 90/10 Si/Zr[b,d]	355	360	. . .	355	330
	90/10 Si/Al	405	355	335	265	245
3	Pt on 90/10 Si/Al[b]	380	320	300	250	225

[a] ±5. [b] Duplicate preparations of catalysts in Table I. [c] ±10. [d] Catalyst was not sulfided.

Table X. Hydrocracking Performance Is Damaged by Regeneration

(Catalyst 3, standard conditions)

	No Regeneration		4 Regenerations[a]	
Total hydrocracking stream time, days	4.4	25.8	2.4	21.5
Hydrocracking Performance[b]				
C_5+ yield, vol. %	107	106.5	107.5	101
Heavy naphtha, vol. %	34	33.5	36	27
Dry gas, wt. %	2.8	3.5	2.3	5.9
Reactor temp., ° F.	815	850	805	875

[a] Regenerations between periods of hydrocracking lasting 6, 3, 3, 3, and 6 days. [b] See footnotes of Table III.

pressure during the steaming does not alter the surface area loss. These results indicate that surface area loss is independent of the hydrogen partial pressure inherent in hydrocracking, and fit the idea that is is caused by steam partial pressure. Conclusions from autoclave experiments may properly be used to forecast results in a hydrocracker.

Surface area loss during steaming is rapid at first, but soon slows down (Table IX). After 10 days at a temperature and steam pressure expected in a hydrocracker (800° F., 35 p.s.i.a.), surface area per gram dropped only a very few square meters per day in most cases. These and other results (*8*) make it likely that surface area loss continually slows down during steaming at fixed temperature and pressure.

Platinum on silica-zirconia lost 23% of its area in 6 days of steaming at 800° F. and 35 p.s.i.a. (Table IX). This result fits reasonably well into Table VII, in which about the same loss was found at 800° F. when hydrocracking charge stocks which would produce about that partial pressure of steam by complete conversion of their combined oxygen to water. Thus, most or all of the oxygen compounds in the charge stocks of Table VII probably were actually converted to steam in the hydrocracker.

Silica-zirconia was impregnated with aqueous cobalt chloride and ammonium molybdate, dried, and calcined to make catalyst 10. During these operations, catalyst area dropped from 610 to 355 sq. meters per gram in the preparation of the specific catalyst of Table IX. This drop, which was greater than that produced by steaming the base for 10 days as in Table IX, stabilized the catalyst so that it lost little, if any, surface area during steaming. In fact, presteaming catalyst bases to areas below the final areas produced by the steaming generally (Table IX) stabilized the bases against rapid loss during those experiments (*8*).

DAMAGE DURING REGENERATION *vs.* DAMAGE DURING HYDROCRACKING

Table VII indicates that damage to surface area comes from steam made in the hydrocracker from combined oxygen in the gas oil, rather than from coke in the regenerator. Table X indicates that some of the damage to hydrocracking performance occurs during regeneration. Table X compares the results of 22 days of gas oil processing interrupted by four regenerations with 26 days of processing without any regeneration. The catalyst here was platinum on 46-AI silica-alumina (No. 3). Clearly, hydrocracking performance deteriorated much more rapidly when the regenerations were practiced. Taken together with the DA and surface area findings, the results suggest that performance damage is done during both on-stream hydrocracking and regeneration. Damage to individual catalyst properties or functions, however, is considerably localized in either the hydrocracking period or the regeneration period in some instances; it may not be in others.

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