JOURNAL OF CATALYSIS **25**, 204–211 (1972)

The Promotional Effect of Water in Hydrocracking

T. Y. YAN

Mobil Research and Development Corporation, Princeton, New Jersey 08540

Received May 4, 1971

The effects of water on the hydrocracking of *n*-hexadecane and of a certain hydrocracking feed using a rare-earth containing X zeolite and an acid Y catalyst have been examined. The results indicate that the partial pressure of water in the reaction system exerts a marked influence on both activity and selectivity which are quite different between the two catalysts tested. The effects manifest themselves quickly and are reversible by drying with hydrogen at 600°F. To explain the observations, three concurrently operating mechanisms are proposed.

INTRODUCTION

In hydrocracking, water is usually present in the reactor. This water comes from several sources: (a) conversion of oxygen compounds in the charge stock during the reaction; (b) water dissolved in the charge stock; and (c) water picked up by the recycle gas from the scrubbers. The steady state water content of a system can be monitored and controlled if warranted. This study is directed to determining the effect of water on the hydrocracking reaction. The parameters examined were (a) the effect of water on catalyst activity and on product yield, and (b) the response of different types of catalyst and charge stock to water addition.

The effect of water on some reactions related to hydrocracking has already been reported. For example, Yamamoto *et al.* (*1*) found that the *n*-pentane isomerization activity of platinum on rare-earth exchanged Y (Pt/REY) catalyst was enhanced by addition of *i*-propanol to the reaction and/or by steam treatment of the catalyst. Huo *et al.* (*2*), in using a pulse technique, reported that water promoted the cracking reaction on type Y zeolites. The catalytic cracking of *n*-hexadecane over silica–alumina is also promoted by addition of steam (*3*). However, the results reported in the literature were obtained at conditions quite different from those of hydrocracking.

EXPERIMENTAL

A. *Catalysts*

1. *Preparation*

a. Palladium on rare-earth exchanged X type zeolite (Pd/REX): The NaX zeolite was exchanged with rare-earth chloride mixtures to a sodium level of 0.8%. The exchanged zeolite was extruded into 3/32 in. particles, dried, and vacuum impregnated to 1% Pd using dilute H_2PdCl_4 solution. The product was dried quickly, and calcined with air at 1000°F.

b. Platinum on acid Y type zeolite (Pt/HY): The NaY zeolite was exchanged repeatedly with NH_4Cl to a sodium level of 0.1%. The exchanged zeolite was dried, and impregnated with Na_2PtCl_6 to 2.5 wt% Pt level. The wet product was heated at 200°F for 3 hr and, finally reduced with H_2 at 900°F. The sodium level of the final catalyst was 0.83 wt%.

2. *Characterization*

The catalysts were tested for the following two functional activities:

a. Cracking activity (α test): This is the relative psuedo-first order reaction rate constant of the acid base for cracking of *n*-hexane. In this activity scale, a typical silica–alumina catalyst was arbitrarily set equal to unity.

b. Hydrogenation activity: This is an indication of relative activity of the hydrogenation component measured as the percentage of benzene hydrogenated at 1 space-velocity, 1 atm and 500°F.

The results are shown below:

Catalyst	Pd/REX	Pt/HY
Base cracking activity	300	500,000
Hydrogenation activity	46.2	1.2

B. *Charge Stock*

1. *n-Hexadecane*

Commercial pure grade was used as received or dried over 4A sieve and filtered as noted.

2. *Commercial Blend*

The raw hydrocracking feed was pretreated over a commercial hydrotreating catalyst to a nitrogen level of ~1 ppm. The raw feed consisted of: light coker gas oil, 18.9 wt%; heavy coker gas oil, 12.2 wt%; light catalytic cracking gas oil, 18.4 wt%; heavy catalytic cracking gas oil; and furfural extract of heavy gas oil, 50.5%.

3. *i-Pentanol*

Commercial grade was used as received.

C. *Operating Procedure*

Ten milliliters of catalyst were charged to a high pressure flow reactor. The reactor was pressured up to the desired unit pressure with H_2. With H_2 flowing, the reactor was heated to ~300°F and the oil pump was started. It is to be noted that no deliberate prereduction was carried out prior to the cracking reaction. The experiment was conducted with single pass operation. A conversion level of about 60% was maintained by adjusting the reactor temperature. The rest of the process parameters are listed below:

Charge stock	*n*-Hexadecane	Commercial blend
Pressure (psi)	500	1500
LHSV* (v/v hr)	1.0	1.0
H_2 Circ. Rate (SCF/B)	7500	7500
H_2/Hydrocarbon at inlet (mol/mol)	16	218

A high pressure water bubbler was installed in the hydrogen gas line and was controlled at the desired temperature to control the water content of the hydrogen stream. A bypass around the water bubbler was installed so that dry hydrogen gas could be used.

Material balances were made to obtain the product distribution.

The catalyst activity was determined by the reactor temperature required to obtain the conversion level of 60 wt%. Obviously, the lower the reactor temperature required, the more active the catalyst is. The catalyst selectivity is defined as follows:

For hydrocracking of hexadecane,

$$\text{Selectivity for Product } i = \frac{\text{Yield of product } i \text{ (wt\%)}}{\text{Conversion of hexadecane (wt\%)}} \times 100.$$

For hydrocracking of the commercial blend,

$$\text{Selectivity for Product } i = \frac{\text{Yield of product } i \text{ (wt\%)}}{\text{Conversion of } T > 390°\text{F stock (wt\%)}} \times 100.$$

RESULTS AND DISCUSSIONS

A. *Hydrocracking of n-hexadecane*

1. *Activity of Pd/REX and Pt/HY*

The activity of Pd/REX and Pt/Hy for hydrocracking dry *n*-hexadecane is shown in Figs. 1 and 2. In the figures, the reactor temperatures required for a conversion level of 60% are plotted against the "on-stream time." The temperature required to maintain this conversion in-

---

[*] LHSV = Liquid hourly space velocity; SCF/B = Standard cubic feet of hydrogen per barrel of feed.

creased, and finally equilibrated after about 20 hr on-stream time. These equilibrium temperatures are considered to be the activity of the catalysts, which were 485 and 440°F for Pd/REX and Pt/HY, respectively. One would expect that in hydrocracking *n*-hexadecane where little hydrogenation activity is required, the acidic cracking function of the catalyst will be rate controlling. Indeed, we found Pt/HY was 45° more active than Pd/REX because the former has a more active cracking base.

2. *Activation of Pd/REX Catalyst by i-Pentanol*

After the Pd/REX catalyst was equilibrated with dry *n*-hexadecane, 3 wt% of *i*-pentanol was added to the charge stock. The catalyst activity was improved and the temperature required for 60% conversion was lowered to 473 vs 485°F for dry *n*-hexadecane as shown in Fig. 1. Translating this temperature improvement using first order reaction kinetics, we find that the rate constant was improved by ~50%. Since *i*-pentanol is easily converted to pentene and water over zeolite catalysts at the conditions used, it was necessary to determine whether pentene or water was the activator.

3. *Activation of Pd/REX with Proper Amount of Water*

As shown in Fig. 1, after 50 hr on-stream time the *i*-pentanol was removed and water was added (310 mm partial pressure) by saturating the hydrogen stream. The catalyst activity was about that observed when dry *n*-hexadecane was charged. Apparently the water concentration was too high and the water competed *too* favorably with *n*-hexadecane for adsorption on the active sites. The catalyst was then dried *in situ* by cutting off the feed and raising the reactor temperature to 600°F for 5 hrs while hydrogen was flowing through. After drying the catalyst, the water content of the hydrogen gas was controlled at 22 mm partial pressure (2.5×10^{-2} mol% of H_2O) and hydrocarbon was charged over the catalyst again. As shown in Fig. 1, the catalyst activity equilibrated again at 473°F as it did when *i*-pentanol was charged. Thus, we established that water is the activator. It is positively demonstrated in section 5 that pentene-2 was not an activator. This conclusion was further supported by the fact that the catalyst activity gained by water was lost by drying the catalyst (see Fig. 1 and compare the 90–160 and the 160–180 hr "on-stream time").

In the experiments in which water was

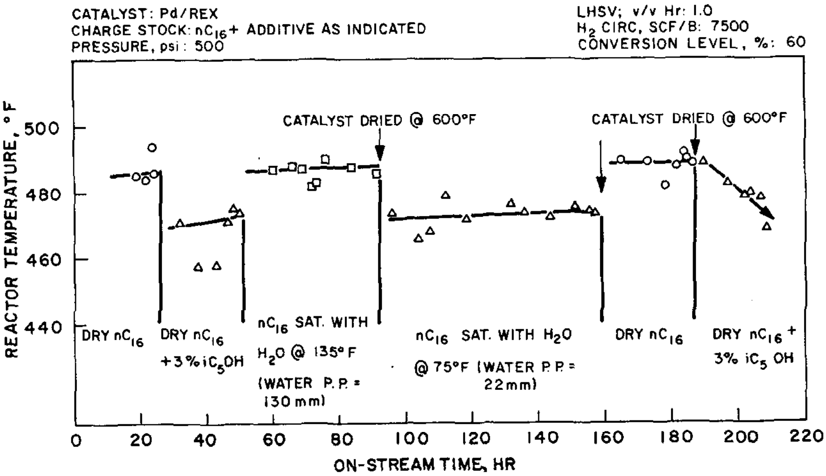

FIG. 1. Effect of water addition on hydrocracking activity of rare-earth containing catalyst.

added, traces of water were always found in the product after the catalyst was equilibrated. Apparently, the equilibrium moisture level between the fluid stream and the catalyst had been established.

The equilibrium content of water on the REX base at 500°F and 22 mm H_2O partial pressure is estimated to be ~7 wt%.

4. *Effect of o-Pentanol on Product Yields from Pd/REX*

The product yields from runs with and without addition of *i*-pentanol are shown in Table 1. We observe that (a) addition of *i*-pentanol increased the *i/n* ratio of the cracked products, i.e., the isomerization activity of the catalyst was enhanced by *i*-pentanol, which is in agreement with that reported by Yamamoto *et al.* (*1*), and (b) the yield of C_4 and lighter products seems to be suppressed by *i*-pentanol. The same observation was made in cracking the commercial blend as will be mentioned later.

5. *Ineffectiveness of Pentene-2 as a Promoter*

As further proof of the identification of the activator, pentene-2 was added to the

TABLE 1
PRODUCT YIELDS FROM HYDROCRACKING OF *n*-HEXADECANE CATALYST: Pd/REX

Product	Yield (raw data wt%)	Selectivity (%)	*i/n* Ratio	Yield (raw data wt%)	Selectivity	*i/n* Ratio
On-Stream Time (days)		1.0			1.56	
Pentanol-2 Added wt%		0.0			3.0	
Temperature (°F)		491			483	
Water Added		No			Yes	
Conversion wt%[a]		54.54			62.39	
C_1	—	—		—	—	
C_2	0.24	0.44		0.33	0.49	
C_3	1.09	2.00		1.70	1.78	
C_4	5.60	12.50		6.76	10.04	
C_5	8.00	14.70		12.33	18.30	
C_6	2.28	4.18		4.38	6.50	
iC_7	2.26	4.14	3.48	3.55	5.27	3.91
nC_7	0.65	1.19		0.91	1.35	
iC_8	4.30	7.88	3.98	5.88	8.74	5.82
nC_8	1.08	1.98		1.01	1.50	
iC_9	5.48	10.06	5.09	6.80	10.10	6.16
nC_9	1.08	1.98		1.11	1.64	
iC_{10}	5.70	10.45	3.78	6.69	9.97	6.08
nC_{10}	1.51	2.77		1.11	1.64	
iC_{11}	5.38	9.87	6.25	6.49	9.62	7.13
nC_{11}	0.86	1.58		0.91	1.35	
iC_{12}	4.52	8.28	6.05	4.77	7.07	6.72
nC_{12}	0.75	1.37		0.71	1.05	
C_{13}–C_{15}	3.76	6.90		2.45	3.64	
iC_{16}	32.46		2.50	23.43		2.56
nC_{16}	13.00			9.18		
Total	100.00			100.00		

[a] Conversion to C_{15} or lighter.

n-hexadecane charge and hydrocracked over Pt/HY catalyst after it was lined out with dry n-hexadecane. Neither promotion nor deactivation effect was found, as shown in Fig. 2.

6. *Deactivation of Pt/HY Catalyst by i-Pentanol and Water*

As shown in Fig. 2, the Pt/HY catalyst was deactivated by 30°F (from 440 to 470°F) when i-pentanol was introduced. The same lower catalyst activity was maintained at 470°F when water was added instead of i-pentanol. It is believed that the catalyst was deactivated because of competition of water for available sites.

7. *Reversibility of the Effect of Water*

The effect of water is reversible. The promotional effect of water on Pd/REX was lost by drying the catalyst at 600°F in a hydrogen stream for 5 hr (see Fig. 1). Conversely water-deactivated Pt/HY catalyst was restored in activity when dried. (See Fig. 2.)

8. *Proposed Explanation for the Effect of Water*

Based on the above experimental results, we concluded that the role of water in hydrocracking systems is as follows:

(a) Water is the activator. Isopentanol was dehydrated to water and pentene according to the following reaction

$$i\text{-}C_5H_{11}OH \rightarrow i\text{-}C_5H_{10} + H_2O$$

(b) Water competes with n-hexadecane very favorably for adsorption on the catalyst so that the *adsorptive* centers available for n-hexadecane are greatly reduced.

(c) Water hydrates the protonic sites originally present in the catalyst to reduce its cracking activity. Mechanisms (b) and (c) explain the deactivation of Pt/HY catalyst by water.

(d) Water activates the REX cracking base by creating additional protonic sites through hydration of the rare-earth ion

$$RE^{3+} + H_2O \rightleftarrows REOH^{2+} + H^+.$$

This is the view advanced first by Plank (*5*) and later by Venuto, Hamilton, and Landis (*6*). This mechanism explains the increased cracking and isomerization activities by water and the *reversibility* of this effect. Apparently, in the case of REX catalyst, the activation by hydration of rare earth by water overcompensates the suppression of activity by surface adsorption and hydration of proton sites.

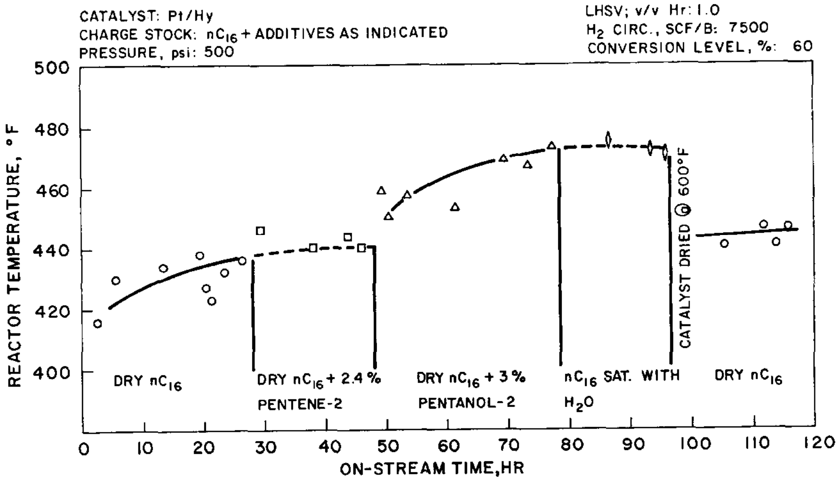

FIG. 2. Effect of water addition on hydrocracking activity of acid Y catalyst.

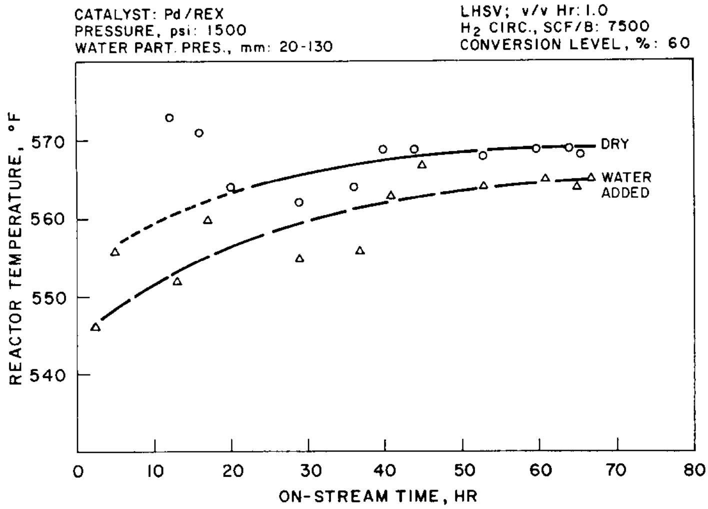

FIG. 3. Effect of water addition on catalyst activity for hydrocracking of the commercial blend.

B. *Hydrocracking of the Commercial Blend*

1. *Effect of Water on Hydrocracking Activity*

The hydrocracking activities of Pd/REX catalyst using the commercial blend with and without water addition are shown in Fig. 3. The activity with water addition was consistently higher than that without water, though the difference amounts to only about 5°F. However, it is worth noting that the activation mechanism (i.e., hydration of the rare earth ion to create protonic sites) still overcame the suppression mechanisms (i.e., water adsorption to occupy the active centers).

Thus, the effectiveness of water addition when hydrocracking the commercial blend was shown to be less than that when hydrocracking *n*-hexadecane. The possible reasons for this are:

(a) There are oxygen compounds in the commercial blend which would be converted into water. As a result there is always some water in the system even when running "dry."

(b) Since the commercial blend contains about 20% aromatics, the hydrocracking rate controlling step may not be the cracking function.

2. *Effects of Water on Product Yields*

The product yields are compared for runs with and without water.

The selectivity, as defined, depends greatly on the conversion level. For ease of comparison, the selectivities for dry gas (i.e., methane, ethane, and propane), for butanes, and for pentanes are plotted in Fig. 4 as function of conversion level. It is seen that the dry gas and the butane

TABLE 2
EFFECT OF WATER ON PRODUCT YIELD FROM COMMERCIAL BLEND

Catalyst: Pd/REX
Pressure (psi) 1500
LHSV (v/v hr) 1.0
H_2/Hydrocarbon (mol/mol) ~17
Conversion to gasoline and lighter (wt%) ~60

Run	A	B
H_2O addition	No	Yes
Product Yield (wt%)		
Methane, ethane, and propane	1.3	0.8
Butanes	9.2	6.5
Pentanes	10.8	7.1
125–180°F light gasoline	3.0	4.0
180–390°F heavy gasoline	38.0	44.0
$T > 390$°F unconverted material	39.7	39.4
Total	102.0	101.8

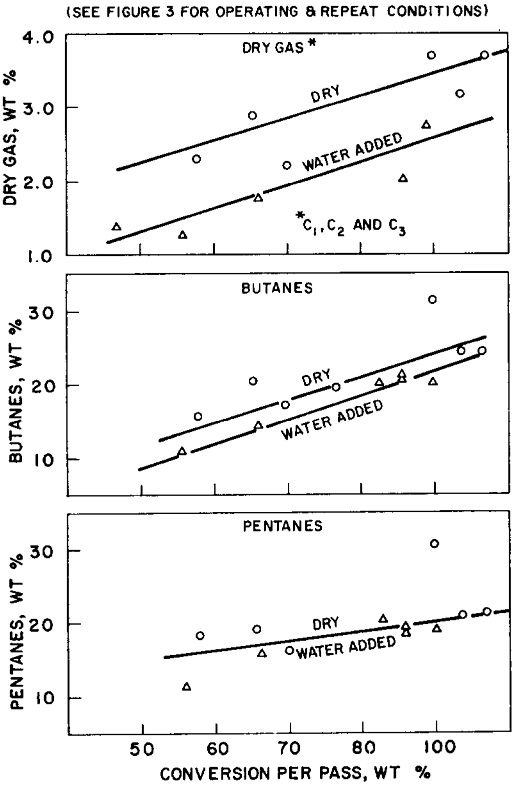

FIG. 4. Effect of water addition on product selectivity commercial blend. (See Fig. 3 for operating and repeat conditions.)

yields were considerably suppressed by water addition. Since the yield of C_5 was about the same in all cases, the reduced yields of dry gas and C_4 will mean an increase in the yield of C_6+ gasoline. In Table 2, the material balances for runs with and without water addition are shown. For the same conversion level of 60 wt%, the total gasoline (125–390°F boiling range) was increased from 41 to 48 wt% when water was added.

CONCLUSIONS

The effects of water and *i*-pentanol on hydrocracking of *n*-hexadecane and a commercial blend over a rare-earth containing zeolite catalyst (Pd/REX) and acid Y type zeolite catalyst (Pt/HY) have been examined.

In hydrocracking *n*-hexadecane, controlled amounts of both *i*-pentanol and water (e.g., 20 mm Hg partial pressure) promoted the activity of Pd/REX catalyst, i.e., rate constants for cracking were increased, and the *i/n* ratios of the cracked products were increased. Under these reaction conditions, *i*-pentanol readily decomposes to water and the olefin. In both cases, the activator is *water*. The optimum amount of water has not been determined, however.

On the other hand, the cracking activity of the Pt/HY catalyst was suppressed by the presence of water.

With either catalyst the effect of water is sustained and reaches a steady state long before the end of the three-day testing period over which the experiments were carried out. The effect is reversible, i.e., the original activity is restored by drying the catalyst with H_2 at 600°F. Based on these results, we propose the following explanation for the effect of water:

(1) The catalyst base is activated by creating more protonic centers through hydration of the rare earth cations.

(2) Water deactivates the catalyst by competing with the hydrocarbons for the surface.

(3) Water deactivates the catalyst by hydrating protons present in the catalyst to diminish acid strength.

The results we observed were the net effects of the three mechanisms. It follows that rare-earth containing catalysts are probably unique in that the activating step (1 above) can more than offset deactivating steps (2 and 3). Only the latter are possible with acid Y type zeolites.

In hydrocracking the commercial blend, the cracking activity of Pd/REX was promoted only slightly (~5°F). However, the light product (C_1, C_2, C_3, and C_4) yields are reduced. For example, at 60% conversion level, dry gas yield was reduced from 2.6 to 1.7 wt% while the C_4 yield was reduced from 15 to 12 wt%.

ACKNOWLEDGMENT

I wish to thank Messrs. S. M. Oleck, E. J. Rosinski, and W. A. Stover of Mobil Research and Development Corporation for providing the catalysts studied.

REFERENCES

1. YAMAMOTO, N., FUJII, K., IDEMARU, Y., AND FURUDAWA, T., *Bull. Jap. Petrol. Inst.* **8**, 13 (1966).
2. HUO, S. T., ROMANOVSKII, B. V., AND TOPECHIEVA, K. V., *Dokl. Akad. Nauk SSSR* **168**, 1114 (1966).
3. PANSING, W. P., *J. Phys. Chem.* **69**, 392 (1965).
4. PLANK, C. J., *in* "Proceedings of the International Congress on Catalysis, 3rd, Amsterdam, 1964," Vol. 1, p. 727. Wiley, New York, 1965.
5. VENUTO, P. B., HAMILTON, L. A., AND LANDIS, P. S., *J. Catal.* **5**, 484 (1966).