JOURNAL OF CATALYSIS **92**, 187–192 (1985)

The Effects of Hydrogen on Cumene Disproportionation and Catalyst Deactivation on a Commercial Hydrocracking Catalyst

The effect of hydrogen on alkylbenzene disproportionation has been the subject of several investigations; however, discrepancies exist. Bhavikath and Patwardhan (*1*) examined the effect of hydrogen on the toluene disproportionation activity of two different catalysts at 400°C and atmospheric pressure and with hydrogen/toluene mole ratio of 5 to 1. On HM(12)—H-Mordenite with a Si : Al ratio of 12—they found that replacing the nitrogen carrier gas with hydrogen did not affect the rate of catalyst deactivation nor the conversion at zero time-on-stream. Gnep and Guisnet (*2*), however, studied the same reaction at 400°C and 15 bars pressure with hydrogen/toluene mole ratio of 4 to 1; they concluded that hydrogen did not affect the disproportionation activity of fluorinated alumina, but did inhibit the activity of various mordenite catalysts. To account for this inhibition Gnep and Guisnet proposed that toluene undergoes a rapid hydride abstraction by a strong Brønsted-acid site to yield a carbenium ion and molecular hydrogen; the effect of hydrogen in the feed stream is thus to displace the equilibrium and inhibit the reaction. In their study of Ni/HM(12), Bhavikath and Patwardhan found that introduction of hydrogen enhanced catalyst stability, but reduced the initial conversion. Similarly, Karge *et al.* (*3*) observed that hydrogen inhibited the disproportionation of ethylbenzene over 0.2 wt% Pt/LaNa*X* at an ethylbenzene mole fraction of 0.013 and a reaction temperature of 423 K at 1 atm pressure, but had no apparent effect on the disproportionation of ethylbenzene over LaNa*X* at similar reaction conditions. Their results were in accord with the hypothesis of Chick *et al.* (*4*) as follows: Hydrogen adsorbs on Pt group metals and the activated hydrogen subsequently spills over onto Lewis-acid sites adjacent to the strong Brønsted-acid sites (hydroxyl groups) required for disproportionation of ethylbenzene. Adsorption of the dissociated hydrogen results in a decrease in acid strength of the neighboring hydroxyl groups and a corresponding decrease in activity of the Pt/LaNa*X* catalyst upon introduction of hydrogen. This interpretation has recently been questioned, however, so the detailed mechanism is not yet resolved (*5, 6*).

In the present work the effect of hydrogen on cumene disproportionation over a typical commercial hydrocracking catalyst containing oxides of Mo and Co is examined. The role of the metal oxides in the disproportionation reaction and the deactivation process is assessed.

EXPERIMENTAL

A conventional once-through flow reactor, operated at conversions less than 10%, was used for experiments at a hydrogen partial pressure of 8.1 atm or a helium partial pressure of 8.5 atm, and at a reaction temperature of 458 K. Details regarding experimental equipment and procedure as well as product distribution are given elsewhere (*7*).

The two similar catalysts examined here (AM-C, NU-D) were supplied by Amoco Oil Company and consist of Co and Mo oxides deposited on a support composed of crystalline aluminosilicates (i.e., zeolites) dispersed in a porous matrix of silica–alumina. BET surface areas for these catalysts were approximately 300 m^2/g. All samples

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were crushed and screened to 0.2 mm average particle size and pretreated with flowing nitrogen for 1 h at each of the following temperatures: 25, 365, 25°C.

EXTRAPOLATION TECHNIQUE

Deactivation occurs during the kinetic experiments, so it is necessary to develop a consistent means of determining fresh catalyst rate data. The initial rate of benzene formation via cumene disproportionation was determined by (i) monitoring conversion as a function of time-on-stream; (ii) fitting the deactivation data to one of two correlations (Eqs. (1) and (2) below); and (iii) calculating the initial rates of reaction using Eqs. (3) and (4).

$$x_2'(t) = x_2'(0)\exp[-at^{0.5}] \tag{1}$$

$$x_2''(t) = x_2''(0)[1 + bt]^{-2} \tag{2}$$

$$r_b'(0) = Fx_2'(0)/W \tag{3}$$

$$r_b''(0) = Fx_2''(0)/W \tag{4}$$

Equation (1) is a modified form of Voorhies correlation proposed by Mahoney (*8*) and Eq. (2) is an hyperbolic form of rather general applicability (*9*).

Parameters of these correlations have been estimated by both linear and nonlinear regression methods (*9, 11*). Very similar results were obtained with both methods and with both types of decay correlation; we present the results of the Voorhies-type relationship here in Table 1.

TABLE 1

Parameter Estimates For The Voorhies-Type Correlation. Experiment 21, Catalyst NU-D

Parameter	Regression method	
	Linear	Nonlinear
$x_2'(0)$	0.0789	0.0794
(90% Confidence interval)	—	3.8%
a	0.0765	0.0772
(90% Confidence interval)	—	5.2%
Sum of squares of residuals		0.157×10^{-5}

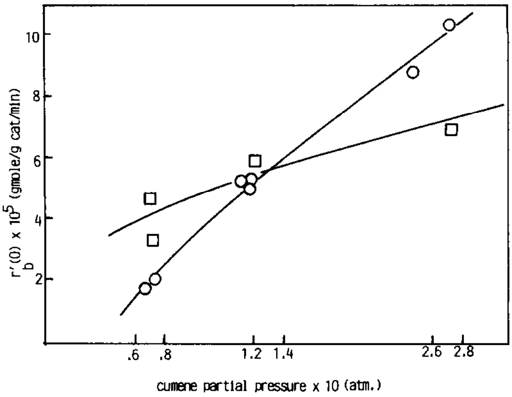

FIG. 1. The effect of hydrogen on $r_b'(0)$ at a reaction temperature of 185°C. ○—Hydrogen, □—helium.

The initial rates of reaction were subsequently fit to the kinetic model

$$r_b(0) = \frac{k_1K_2^2P_c^2}{[1 + K_2P_c]^2} \tag{5}$$

detailed previously (*9, 10*), using nonlinear regression.

RESULTS

A series of experiments were performed over catalyst NU-D at various cumene partial pressures in helium or hydrogen (8.5 or 8.1 atm, respectively) at 185°C. The results plotted in Fig. 1 indicate that the effect of hydrogen on the rate of cumene disproportionation depends on the cumene partial pressure. At low cumene pressures introduction of hydrogen in place of helium inhibits the reaction, while at elevated cumene pressures introduction of hydrogen promotes the reaction. The parameters in the kinetic model were estimated and are

TABLE 2

Effect of Hydrogen on Kinetic Parameters at 185°C Based on $r_b'(0)$

Carrier gas	Rate equation parameters	
	k_1 (g mole/g cat/min)	K_2 (atm^{-1})
Hydrogen	0.303×10^{-3}	0.503×10^{1}
Helium	0.839×10^{-4}	0.309×10^{2}

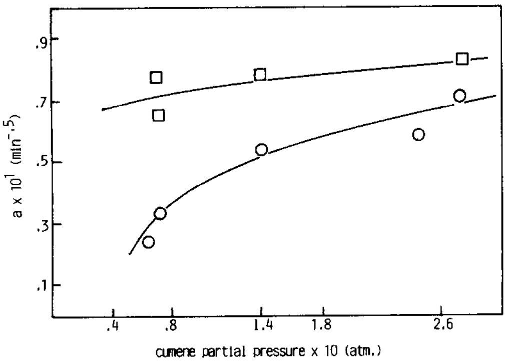

FIG. 2. The effect of carrier gas and cumene partial pressure on deactivation at a reaction temperature of 185°C. ○—Hydrogen, □—helium.

listed in Table 2. As shown, when hydrogen is used as the carrier gas k_1 is increased by a factor of almost 4 while K_2 is reduced by a factor of about 6 compared to helium.

In Fig. 2 the deactivation parameter "a" defined in Eq. (1) has been plotted as a function of cumene partial pressure and carrier gas. Clearly, when hydrogen is used as carrier gas the rate of catalyst deactivation is reduced, i.e., "a" decreases.

To ascertain the role of the metal functions, the initial rates of reaction and the deactivation parameters of fresh catalyst AM-C and the acidic support without metals were determined. The experimental conditions and results listed in Table 3 reveal that the metal oxides apparently did not play any role in the mechanism of cumene disproportionation or in the deactivation process. The metal oxides also exhibited no activity for cumene hydrogenation to isopropylcyclohexane.

DISCUSSION

The negligible effect of metal oxides on the deactivation process is somewhat surprising since one reason for the use of metals in hydrocracking catalysis is to impart a relatively strong hydrogenation activity in order to enhance catalyst stability, as summarized by Beuther and Larson (*12*).

Two possible explanations for the inactivity of the hydrogenation function are a follows: First, the function may quite possibly be inactive because the metallic oxides are not reduced to a hydrogenation-active form under the experimental conditions used here. Second, the acidic sites may be too far removed from the hydrogenation sites to be affected by them, if they are indeed active. While the exact procedure employed to prepare these commercial hydrocracking catalysts is proprietary, it is known that the oxides of the molybdenum are located in the pores of the amorphous silica–alumina matrix, not in the zeolite cages. The location of the cobalt oxides is not clear, however, they would be expected to be associated with the molybdenum oxide in the pores of the matrix (*13*). It is probable that the sites active for cumene disproportionation are predominantly associated with the zeolite component of the catalyst. Typically, a zeolite catalyst has an activity four orders of magnitude larger than amorphous silica–alumina (*14*). Consequently, if the hydrogenation function is located in the pores of the silica–alumina matrix and if the major contribution to cumene disproportionation activity is made by the zeolite component, then the acidic sites are simply too far removed from the hydrogenation sites to be affected by them. However, this view does not account for

TABLE 3

Effect of Presence of Oxides of Cobalt and Molybdenum on Catalyst Deactivation

Conditions and parameters	Catalyst	
	AM-C	Acidic support
Temperature (°C)	182	182
Hydrogen pressure (atm)	7.70	7.60
Cumene pressure (atm)	0.138	0.138
Number of replicate experiments	3	4
$a \times 10$ (min$^{-0.5}$)	0.611	0.625
$r_b'(0) \times 10^{-4}$ (g mole/g cat/min)	8.67	8.44

the decrease in the rate of deactivation upon introduction of hydrogen.

Wolf and Alfani (*15*) concluded that the mechanism of coke formation involves a multistep reaction sequence consisting of dehydrogenation followed by condensation, polymerization, and cyclization of the hydrogen-deficient fragments. Such fragments can be produced to a small extent by a slight amount of cumene dealkylation (to yield propylene and benzene) accompanying disproportionation. They can also be formed via the dual nature of the Brønsted-acid sites. Such sites are both adsorption sites and as well, their acidic nature can induce hydrogen elimination (*16*) by reaction sequences as illustrated in Fig. 3. If the adsorption step is at equilibrium, then introduction of hydrogen displaces the equilibrium and inhibits the formation of species CP, a possible coke precursor, so the rate of deactivation decreases.

The explanation given by Karge *et al.* (*3*) cannot be applied to account for the effect of hydrogen on the rate of cumene disproportionation because the hydrogenation function appears not to affect either the rate of cumene disproportionation nor the deactivation process. Rather, the inhibiting effect of hydrogen on cumene disproportionation at low cumene partial pressures can be explained by an adsorption step involving a strong Brønsted-acid site to form the carbenium ion and molecular hydrogen as illustrated in

$$
\begin{array}{lll}
\text{(i)} & 2[\mathrm{C} + \mathrm{S} \rightleftharpoons \mathrm{CS} + \mathrm{H_2}, & L_2] \\
\text{(ii)} & 2\mathrm{CS} + \mathrm{H_2} \rightarrow \mathrm{I_1S} + \mathrm{S}, & l_2 \\
\text{(iii)} & \mathrm{I_1S} \rightleftharpoons \mathrm{I} + \mathrm{S} & \quad (6) \\
\text{(iv)} & \mathrm{I} + \mathrm{S} \rightleftharpoons \mathrm{I_2S} & \\
\text{(v)} & \mathrm{I_2S} \rightleftharpoons \mathrm{B} + \mathrm{DS} & \\
\text{(vi)} & \mathrm{DS} + \mathrm{H_2} \rightleftharpoons \mathrm{D} + \mathrm{S} &
\end{array}
$$

Again, if the adsorption step is assumed to be at equilibrium, then introduction of hydrogen displaces the equilibrium so that the fraction of the covered surface decreases, and thus the rate of reaction. To account for an increase in the rate of reaction at higher cumene partial pressures, one can propose that hydrogen is involved in the surface reaction as illustrated in Eqs. (6i, ii). These two reactions are the first steps in the working model proposed previously (*9*). For irreversible rate-controlling surface reaction and negligible product inhibition, a Langmuir–Hinshelwood analysis of the reaction sequence in Eq. (6) yields the rate equation

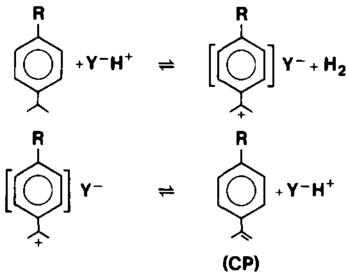

FIG. 3. Adsorption-surface reaction sequence.

$$r'_b(0) = \frac{l_2 P_h [L_2/P_h]^2 P_c^2}{[1 + (L_2/P_h)P_c]^2}. \tag{7}$$

By comparison with Eq. (5), it follows that

$$k_1 = l_2 P_h \tag{8}$$

$$K_2 = L_2/P_h. \tag{9}$$

The effective hydrogen partial pressure P_h will depend on both the presence of hydrogen in the feed stream and the equilibrium constant of surface reaction (6i). However, it is clear that P_h is smaller when helium is used as carrier gas instead of hydrogen. Thus the working kinetic model predicts that

$$k_{1,h} > k_{1,he} \tag{10}$$

$$K_{2,h} < K_{2,he} \tag{11}$$

The predictions are consistent with the experimental observations presented in Table 2.

Because of the experimental errors involved in extrapolating to zero time on stream, we have not made a detailed quantitative analysis of these effects. However, the working model is able to predict, at least qualitatively, the effects of hydrogen on alkylbenzene disproportionation in these experiments.

In summary, the development given above, together with the model proposed previously (*9*), (i) permits the development of a decay correlation that fits the deactivation data very well and yields estimates of initial conversions, (ii) allows the initial rate data to be readily correlated with cumene partial pressure and temperature, (iii) predicts, qualitatively, the effect of the introduction of hydrogen on the initial rate of reaction, and (iv) is consistent with the reaction mechanism for alkylbenzene disproportionation in acidic solution (*11*).

From an engineering point of view this is satisfying but it must be remembered that the mechanistic implications are not unequivocally established by kinetics alone. In particular, it would appear that a number of elementary steps are lumped into the surface reaction step which as written appears to be both trimolecular and to require two adjacently adsorbed carbenium ions.

NOMENCLATURE

a	Deactivation parameter in the Voorhies-type correlation, Eq. (1), $\min^{-0.5}$
b	Deactivation parameter in the hyperbolic correlation, Eq. (2), $\min^{-1}$
B	Gas-phase benzene molecule
C	Gas-phase cumene molecule
CP	Gas–phase possible coke precursor molecule
CS	Adsorbed cumene molecule
D	Gas-phase molecule of diisopropylbenzene
DS	Adsorbed molecule of diisopropylbenzene
F	Cumene molar flow rate, g mole/min
I	Gas-phase reaction intermediate for cumene disproportionation—Ref. (9)
I_1, I_2	Adsorbed intermediates of I, Ref. (9)
k_1	Forward rate constant defined in Eq. (6), g mole/g cat/min
$k_{1,h}$	k_1 determined using hydrogen as carrier gas
$k_{1,he}$	k_1 determined using helium as carrier gas
K_2	Adsorption equilibrium coefficient for species CS defined in Eq. (6)
$K_{2,h}$	K_2 determined using hydrogen as carrier gas
$K_{2,he}$	K_2 determined using helium as carrier gas
l_2	Rate constant defined in Eq. (6)
L_2	Adsorption equilibrium coefficient defined in Eq. (6)
P_c	Cumene partial pressure, atm
P_h	Hydrogen partial pressure, atm
$r_b(0)$	Initial rate of benzene formation via cumene disproportionation, g mole/g cat/min
$r'_b(0)$	$r_b(0)$ determined by the Voorhies-type decay correlation, g mole/g cat/min
$r''_b(0)$	$r_b(0)$ determined by the hyperbolic decay correlation, g mole/g cat/min
S	Strong Brønsted site defined in Eq. (6)
t	Time-on-stream, min
$x'_2(t)$	Fraction of cumene converted to benzene via disproportionation as determined by Voorhies-type decay correlation
$x''_2(t)$	Fraction of cumene converted to benzene via disproportionation as determined by hyperbolic decay correlation
W	Mass of catalyst charged to reactor, g

ACKNOWLEDGMENTS

This research was supported by the Amoco Oil Company. Assistance of the Stauffer Chemical Company is also acknowledged.

REFERENCES

1. Bhavikath, S. S., and Patwardhan, S. R., *Ind. Eng. Chem. Prod. Res. Dev.* **20,** 102 (1981).
2. Gnep, N. S., and Guisnet, M., *Appl. Catal.* **1,** 329 (1981).
3. Karge, H. G., Sarbak, Z., Hatada, K., Wetkamp, J., and Jacobs, P. A., *J. Catal.* **82,** 236 (1983).
4. Chick, D. J., Katzer, J. R., and Gates, B. C., "Proceedings, 4th International Conference on Molecular Sieves (J. Katzer, Ed.), p. 515. Amer. Chem. Soc., Washington, D.C., 1977.
5. Guisnet, M., *J. Catal.* **88,** 249 (1984).

6. Karge, H. G., Wada, Y., Weitkamp, J., and Jacobs, P. A., *J. Catal.* **88,** 251 (1984).

7. Absil, R. P. L., M.S. thesis, Northwestern University, Evanston, Ill., 1982.

8. Mahoney, J. A., *J. Catal.* **32,** 247 (1974).

9. Absil, R. P. L., Butt, J. B., and Dranoff, J. S., *J. Catal.* **85,** 415 (1984).

10. Absil, R. P. L., Butt, J. B., and Dranoff, J. S., *J. Catal.* **87,** 530 (1984).

11. Absil, R. P. L., Ph.D. dissertation, Northwestern University, Evanston, Ill., 1984.

12. Beuther, H., and Larson, O. A., *Ind. Eng. Chem. Process Des. Dev.* **4,** 177 (1965).

13. Gutberlet, L. C., Amoco Oil Company, private communication (1984).

14. Haynes, H. W., *Catal. Rev.-Sci. Eng.* **17**(2), 273 (1978).

15. Wolf, E. E., and Alfani, F., *Catal. Rev.-Sci. Eng.* **24**(3), 329 (1982).

16. Eisenbach, D., and Gallei, E., *J. Catal.* **56,** 377 (1979).

R. P. L. ABSIL
J. B. BUTT
J. S. DRANOFF

Department of Chemical Engineering
and Ipatieff Laboratory
Northwestern University
Evanston, Illinois 60201

Received August 16, 1984