JOURNAL OF CATALYSIS 3, 113–122 (1964)

Cumene Cracking Catalyzed by Impregnated and Cogelled Silica-Alumina*

WILLIAM BOYD HORTON AND RUSSELL W. MAATMAN†

From the Department of Chemistry of The University of Mississippi, University, Mississippi

Received August 27, 1963

Cumene cracking catalyzed by silica-alumina in a differential reactor was studied from 390–500°C at cumene partial pressures from 0.06–1.00 atm. Four low aluminum concentration catalysts were made by impregnation; a fifth of much higher aluminum concentration was prepared by cogelling. The results are consistent with the rate law given by Prater and Lago; some of the rate law constants were determined. Active sites in the different impregnated catalysts are of the same type, and their number is directly proportional to aluminum concentration. There are fewer, but more active, sites in the cogelled catalyst. If the pre-exponential factor of absolute rate theory holds, then less than 0.01% of the aluminum atoms are associated with active sites in all the catalysts.

INTRODUCTION

Hydrocarbon cracking catalyzed by silica-alumina has been investigated both with respect to the nature of the active site and the reaction path. Several suggestions concerning the nature of the active site have been made. Thomas (*1*) and Hansford (*2*) suggested that active site acidity is Bronsted acidity, with a proton in the vicinity of a surface aluminum atom. Milliken, Mills, and Oblad (*3*) proposed that catalytic acidity is Lewis acidity associated with surface aluminum atoms. Some have held that both kinds of acidity are related to the catalytic properties of silica-alumina. Catalytic activity has been related to the formation of radical chains (*4*) and, when the catalyst was preirradiated, to the formation of trapped electrons or positive holes (*5*).

Active site and reaction path studies have often been made using cumene (isopropylbenzene) because benzene and propylene are the primary and essentially the only products (*6*). Weisz and Prater (*7*) and Prater and Lago (*8*) reviewed earlier work and studied the reaction; they concluded the kinetic scheme is, in the absence of inhibitor,

$$S + A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} SA \xrightarrow{k_3} \text{products} \qquad (1)$$

where S represents the substrate, cumene, A the active site, and SA cumene adsorbed on the active site. It was assumed that adsorption sites are independent of each other, that cumene cracks while adsorbed, and that conversion is kept low enough (in a flow-type reactor) to render the recombination of products a negligible factor. Then the steady state rate law is

$$dn/dt = k_3 B_0 [P_s/P_s + G)] \qquad (2)$$

where dn/dt is the rate products appear, B_0 is the number of active sites per unit weight or area, P_s is the partial pressure of cumene, and $G = (k_2 + k_3)/k_1$.

Prater and Lago (*8*) reported values for

---

[*] Taken from the thesis of William Boyd Horton presented to the faculty of The University of Mississippi in partial fulfillment of the requirements for the M.S. degree.

[†] Present address: Dordt College, Sioux Center, Iowa.

k_3B_0 and G, and for the temperature coefficients of these quantities, for a cogelled silica-alumina catalyst containing 10 wt % Al_2O_3. A silica-alumina catalyst can also be made by impregnating silica gel with an aqueous solution of an aluminum salt, drying the gel, and finally calcining it (*9*). It is of interest to know how such catalysts compare kinetically with those of the type Prater and Lago studied. In this article results of a kinetic study similar to theirs, but including impregnated catalysts of low aluminum concentration, are reported.

For the impregnated catalysts Eq. (2) is shown to be an adequate rate law. It is shown that the number of active sites is directly proportional to aluminum concentration in the impregnated catalysts. The active sites of the cogelled catalyst in the group studied seem to be qualitatively different from those of the impregnated catalysts. It is concluded for both types that only a very small fraction of the aluminum atoms are associated with activity.

EXPERIMENTAL

Materials. The cumene used was Phillips Pure Grade, 99 mole % minimum. Chromatographic analysis of the cumene as received showed no traces of impurities of molecular weight higher than cumene. It was vacuum-distilled at 27°C, using a 10-inch column packed with glass helices. The fraction used was that which exhibited the highest cracking rate, the last third. It was then stored under nitrogen, to prevent formation of cumene hydroperoxide, a source of catalytic inhibitor (*10*), and used within 5 days. Proof from the rate studies that the cumene was satisfactorily pure is given in the Results and Discussion section.

The cyclopentane used was Matheson, Coleman, and Bell Spectroquality Reagent, with UV absorption at 210 millimicrons reported by the manufacturer. It was stored under nitrogen.

Silica gel used to prepare the catalysts was Davison Code 40, 6-12 mesh, acid-washed, then water-washed, dried, and calcined in air at 450°C for 2 hours, according to the procedure described earlier (*11*). The gel pore volume (by water absorption) is 0.40 ml/g and the BET surface area is 498 m^2/g. To make a catalyst 25 ml of an aluminum nitrate solution was in contact with 15 g of the gel for 2 days, with frequent shaking. Aluminum determinations (easily made by back titrations of EDTA with $ZnCl_2$, since the previous acid wash of the gel removed foreign cations) of the stock solution and the equilibrium solution (i.e., the solution in contact with the gel particles) were used to calculate by difference the amount of aluminum in the pores of the gel; this was possible because the pore volume was known. The gel particles were separated from the equilibrium liquid, blotted, dried at 110°C for 4 hours, and powdered to 100–200 mesh. Just before use the catalyst was heated at 450°C for 20 min in an oxygen stream, cooled, transferred to the reactor, and heated at 450°C for 20 min in a nitrogen stream.

The cogelled catalyst was Mobil silica-alumina, 10 wt % Al_2O_3, with a BET surface area of 393 m^2/g.

Determination of catalytic activity. The flow-type reactor used (Fig. 1) is a modification of the type described by Prater and Lago (*8*). Instead of measuring rates by the pressure increase due to propylene production, the ratio between the benzene and cumene collected by condenser H was determined chromatographically. The cumene flow rate, 30–40 ml/hr, was controlled by controlling the rate of flow from the separatory funnel J and the temperature of the heater A. In almost all runs there was less than 0.1 g catalyst (on tray E), and therefore the liquid hourly space velocity was at least 300.

Usually 30 min after cumene contacted the catalyst the first liquid sample was collected over a 1-min period, and three more samples were collected at 10-min intervals. The liquids were weighed and then analyzed by gas chromatography on an Aerograph Manual Temperature Programmer Model A-90-P, using a Model S-R Sargent recorder.

Cumene partial pressures less than 1 atm

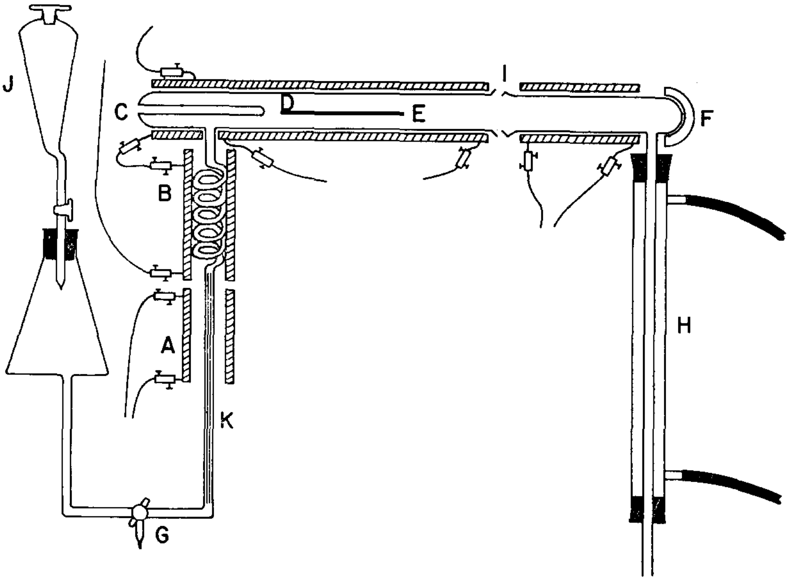

FIG. 1. Differential gas phase reactor. A, boiling heater; B, preheater; C, thermocouple well; D, main reaction chamber; E, catalyst tray; F, asbestos cap; G, 3-way stopcock; H, 12-inch water condenser; I, ground glass joint with clamp; J, cumene reservoir; K, capillaries.

were obtained by dilution with cyclopentane. Cyclohexane does not compete with cumene for active sites (*8*); the assumption that cyclopentane does not compete is consistent with the kinetic analysis in Results and Discussion. Cyclohexane dilution was not used because it interfered in chromatographic analysis. Analyses on cyclopentane-cumene mixtures taken simultaneously from the cumene reservoir and the condenser output showed there was no fractionation in the reactor.

The reaction rates, flow rates, reactor diameter, etc., were such that the criteria for the absence of diffusion effects given by Weisz and Prater (*7*) were met in all runs. In a blank run at 420°C with pure cumene, but no catalyst, there was no thermal cracking.

RESULTS AND DISCUSSION

Summary of rates. The slow attainment of a steady state, also reported by Prater and Lago (*8*), is shown for a typical run in Fig. 2. The steady state rate at 60 min is the rate referred to in this section. These

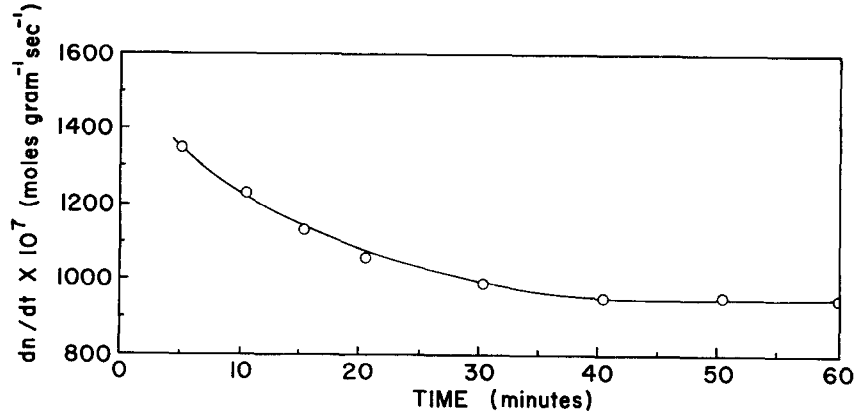

FIG. 2. Time dependence of cracking rate at 420°C, using 0.0091 g cogelled catalyst at $P_s = 1$.

TABLE 1
CRACKING RATE FOR FIVE CATALYSTS

Temp. (°C)	N_{cumene}[a]	$dn/dt \times 10^7$ (moles/g sec)[b]
	Cogelled catalyst	
420	1.0000	958
420	0.7152	779
420	0.5011	603
420	0.2631	360
450	1.0000	1575
450	0.7152	1255
450	0.5011	944
450	0.2631	564
480	1.0000	2490
480	0.7152	1949
480	0.5011	1460
480	0.2631	827
500	1.0000	3442
500	0.7152	2645
500	0.5011	1952
500	0.2631	1116
	Catalyst I[c]	
300	1.0000	20
330	1.0000	48
360	1.0000	98
390	1.0000	203
390	0.7152	195
390	0.5011	169
390	0.2631	119
420	1.0000	355
420	0.7152	311
420	0.5011	287
420	0.2631	191
450	1.0000	685
450	0.8339	577
450	0.6906	599
450	0.5725	524
450	0.4058	381
450	0.2950	297
450	0.1825	196
450	0.0628	77
480	1.0000	1047
480	0.7152	876
480	0.5011	628
480	0.2631	381
500	1.0000	1443
500	0.7152	1128
500	0.5011	844
500	0.2631	484
	Catalyst II[c]	
420	1.0000	230
420	0.7152	202
420	0.5011	181
420	0.2631	110
450	1.0000	404
450	0.7152	338
450	0.5011	245
450	0.2631	169
480	1.0000	649
480	0.7152	525
480	0.5011	381
480	0.2631	238
500	1.0000	850
500	0.7152	659
500	0.5011	517
500	0.2631	283
	Catalyst III[c]	
420	1.0000	189
420	0.7152	151
420	0.5011	132
420	0.2631	96
450	1.0000	286
450	0.7152	237
450	0.5011	186
450	0.2631	125
480	1.0000	512
480	0.7152	405
480	0.5011	322
480	0.2631	183
500	1.0000	711
500	0.7152	549
500	0.5011	449
500	0.2631	226
	Catalyst IV[c]	
420	1.0000	52
420	0.7152	48
420	0.5011	41
420	0.2631	25
450	1.0000	93
450	0.7152	83
450	0.5011	64
450	0.2631	34
480	1.0000	152
480	0.7152	121
480	0.5011	94
480	0.2631	53

TABLE 1 (*Continued*)

Temp. (°C)	N_{cumene}[a]	$dn/dt \times 10^7$ (moles/g sec)[b]
500	1.0000	208
500	0.7152	160
500	0.5011	118
500	0.2631	70

[a] N_{cumene} = mole fraction of cumene in liquid feed.

[b] Catalyst weights varied from 12 to 200 mg; conversions varied from 0.50–2.90 mole % benzene.

[c] Catalysts I, II, III, and IV were 0.322, 0.229, 0.143, and 0.0488 wt % Al, respectively.

rates for the five catalysts, several temperatures, and several cumene partial pressures are given in Table 1.

Determination of G and k_3B_0 of Eq. (2). Rearranging Eq. (2),

$$\frac{dn}{dt} = k_3B_0 - G\frac{dn/dt}{P_s} \qquad (3)$$

Thus the slope of a plot of dn/dt vs. $(dn/dt)/P_s$ is $-G$ and the intercept is k_3B_0. Least-mean-square plots for the cogelled catalyst, typical of all the plots, are shown in Fig. 3 for four temperatures. Values of G and k_3B_0 for all five catalysts at all temperatures are given in Table 2.

The values of G obtained for the cogelled catalyst indicate that the cumene used is free of significant amounts of inhibitor impurities. This is concluded because the presence of inhibitor leads to an abnormally large value of G (*8, 10*), and the value of G reported here is about the same as the value Prater and Lago gave for a similar catalyst using extremely pure cumene.

In the earlier work it was shown that G is essentially the reciprocal of the equilibrium constant for adsorption on active sites. The values of G in Table 2 indicate that with respect to adsorption on active sites the different impregnated catalysts are alike, but different from the cogelled catalyst.

Exponential and pre-exponential factors of G and k_3B_0. Since G is essentially an equilibrium constant, it is of the form

$$G = A_G \exp(-Q_G/RT) \qquad (4)$$

where A_G is temperature-independent and Q_G is the heat of reaction for adsorption on active sites (*8*). Least-mean-square plots of log G vs. $1/T$ (Fig. 4, where all points are given but only one impregnated catalyst curve is shown to avoid confusion) are linear and the values of A_G and Q_G, from the intercept and slope, are given in Table 3.

TABLE 2

G AND k_3B_0 FOR FIVE CATALYSTS

	Temp. (°C)	G (atm)[a]	$k_3B_0 \times 10^7$ (moles/g sec)[b]
Cogelled	420	1.48	2384
	450	1.79	4386
	480	2.54	8859
	500	2.93	13478
Catalyst I	390	0.27	259
	420	0.41	504
	450	1.10	1437
	480	1.71	2852
	500	2.44	5044
Catalyst II	420	0.58	370
	450	0.94	764
	480	1.62	1686
	500	2.24	2754
Catalyst III	420	0.47	264
	450	1.28	677
	480	1.69	1379
	500	1.93	2043
Catalyst IV	420	0.47	76
	450	1.27	217
	480	1.93	447
	500	2.38	694

[a] Standard deviation: ±0.02.

[b] Standard deviation: ±50.

If k_3B_0 is expressed as

$$k_3B_0 = A_k \exp(-Q_k/RT) \qquad (5)$$

A_k is essentially temperature-independent if B_0 is temperature-independent. Plots of log k_3B_0 vs. $1/T$ (Fig. 5) are linear. (The cogelled catalyst is not on the scale of the figure.) Values of A_k and Q_k are given in Table 4. The Q_k values of the impregnated catalysts are almost identical, but significantly different from the value for the cogelled catalyst, once again indicating a fundamental difference in the two types of catalyst.

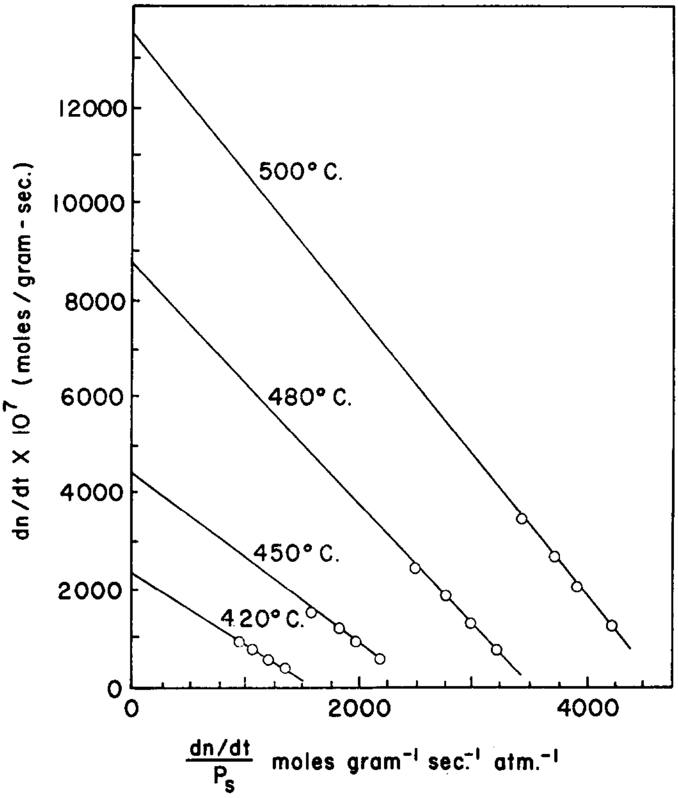

FIG. 3. Determination of G and k_3B_0 at four temperatures for the cogelled catalyst (see text).

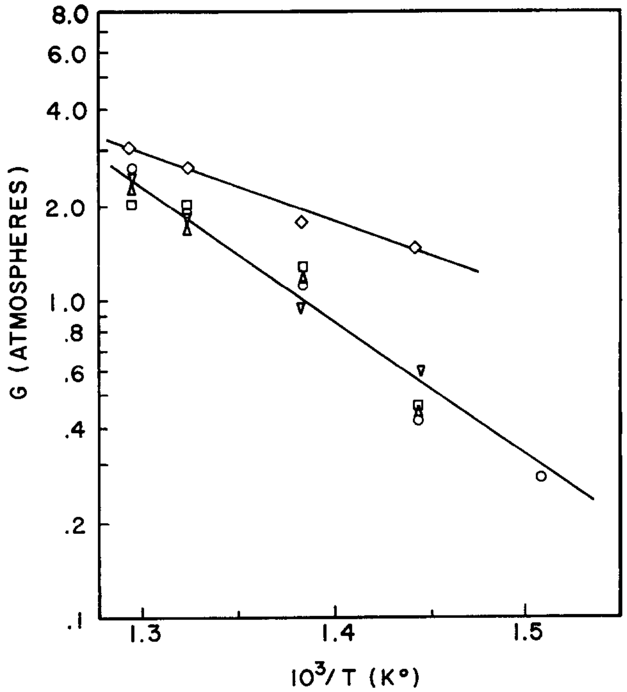

FIG. 4. Log G vs. $1/T$; ◇, cogelled; ○, ▽, □, △ for catalysts I, II, III, and IV, respectively.

TABLE 3
G VALUES[a]

Catalyst	A_G (atm)	log A_G	$Q_G \times 10^{-3}$ (cal/mole)
I	2.44×10^6	6.39 ± 0.93	21.2 ± 0.7
II	0.28×10^6	5.44 ± 0.18	18.0 ± 0.1
III	0.34×10^6	5.34 ± 1.31	18.3 ± 1.0
IV	2.47×10^6	6.39 ± 1.01	21.1 ± 0.7
Cogelled	1.45×10^3	3.16 ± 0.20	9.5 ± 0.2

[a] With standard deviations.

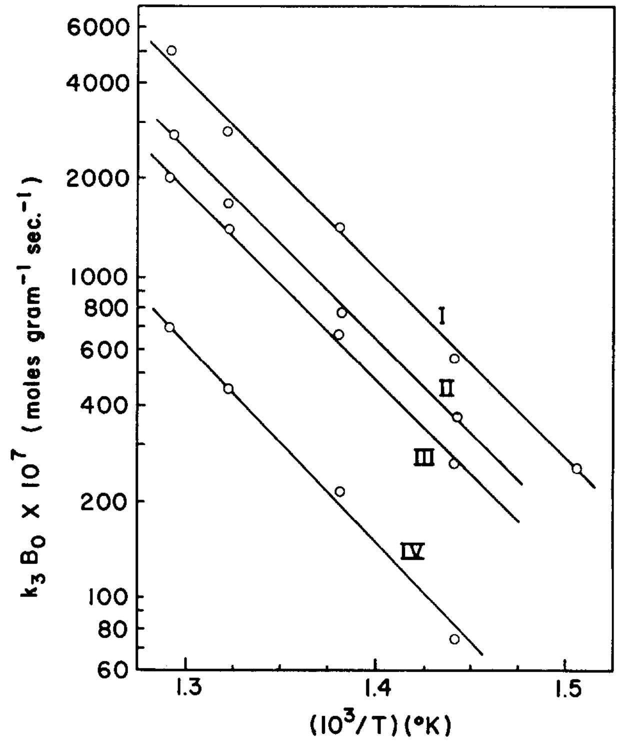

FIG. 5. Log k_3B_0 vs. $1/T$ for impregnated catalysts.

TABLE 4
k_3B_0 VALUES[a]

Catalyst	A_k (moles/g sec)	log A_k	$Q_k \times 10^{-3}$ (cal/mole)
I	3.36×10^4	4.53 ± 0.40	27.7 ± 0.3
II	1.27×10^4	4.11 ± 0.35	27.1 ± 0.3
III	1.28×10^4	4.11 ± 0.38	27.5 ± 0.3
IV	1.67×10^4	4.22 ± 0.43	29.5 ± 0.3
Cogelled	5.45×10^3	3.74 ± 0.26	23.4 ± 0.2

[a] With standard deviations.

The number of active sites. From absolute reaction rate theory the pre-exponential factor in a zero-order surface reaction can be predicted (*12*). Equation (5) becomes, since the k_3 step is zero-order, and since the probable value of the transmission coefficient is unity,

$$k_3B_0 = A_k \exp(-Q_k/RT) = B_0(kT/h) \exp(-Q_k/RT) \quad (6)$$

where k and h are the Planck and Boltzmann constants. (If the transmission coefficient were lower, the calculated B_0 would be higher.) Since Q_k appears to be the same for the impregnated catalysts, the average value was used to calculate new A_k values and B_0 values for those catalysts.

Figure 6 shows the dependence of B_0 calculated in this way upon the aluminum concentration in the impregnated catalysts. Values of B_0 calculated using the individual Q_k values are given in Table 5. [Prater and Lago (*8*) reported about 10^5 times as many active sites per unit area as are reported here for the cogelled catalyst, in a study on a similar catalyst. However, Lago has reported (*13*) newer data in essential agreement with the smaller value. Other estimates concerning numbers of sites or "per cent of surface covered"—see, for example, ref. (*14*)—are, although large, usually not in conflict with the small value reported here because these estimates are usually upper limits.]

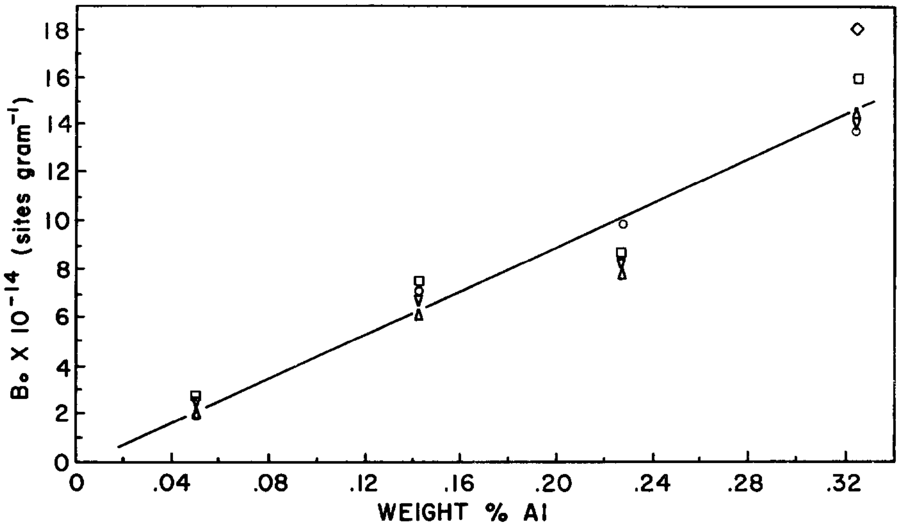

FIG. 6. Number of active sites vs. wt % Al; ◇, 390°C; ○, 420°C; □, 450°C; ▽, 480°C; △, 500°C.

TABLE 5
SITE ACTIVITY FOR FIVE CATALYSTS

Wt % Al	No. active sites × 10^{-15} [a]	Active Al (%)[b]	$(dn/dt) \times 10^7$ (moles/g sec)[c]	Turnover number ($\times 10^{-4}$)[d]
0.322	1.4	1.9×10^{-3}	355	1.5
0.229	0.53	1.0×10^{-3}	230	2.6
0.143	0.53	1.7×10^{-3}	189	2.1
0.0488	0.70	6.4×10^{-3}	52	0.4
5.29[e]	0.23	1.9×10^{-5}	948	25

[a] Number of active sites per gram at 420°C (B_0).

[b] Per cent of aluminum atoms present which are active, assuming one atom per site.

[c] Rate at 420°C and $P_s = 1$ atm.

[d] *Molecules reacting per site per second.*

[e] The cogelled catalyst; 10 wt % Al_2O_3.

If Q_k is truly constant in the impregnated catalyst group, then the number of active sites is proportional to the aluminum concentration in the impregnated catalysts (Fig. 6). The details of the impregnation process are of interest here. When the aluminum nitrate solution penetrates the pores, some aluminum exchanges with the hydrogen of the weakly acidic surface silanol group. However, at equilibrium some of the aluminum is dissolved in the pore volume liquid but not exchanged. Both "kinds" of aluminum are included in the aluminum content of the finished catalyst. The per cent of the aluminum present which exchanged with the surface silanol group has been determined for these four catalysts by a method described previously (*11*). The weight per cent aluminum in the catalyst and the per cent of the amount present which had exchanged, respectively, are: 0.0488, 19.4; 0.143, 8.0; 0.229, 5.6; 0.322, 4.4. Evidently the number of sites is proportional to the aluminum concentration even though there is considerable variation in the fraction of the aluminum which had exchanged before the catalyst was dried.

According to the method used to calculate B_0 for Table 5, there are fewer active sites in the cogelled catalyst than in any of the impregnated catalysts; according to the method used for Fig. 6, only one of the four impregnated catalysts has as small a number of active sites as the cogelled catalyst. Yet the cogelled catalyst is the most active; the number of molecules reacting per site per second (the "turnover number"), while extremely high for all the catalysts, is highest for the cogelled catalyst. This is another way of deducing from the kinetic data that the sites on the two kinds of catalyst are qualitatively different.

Since the cogelled catalyst is by far the most active [greater activity of cogelled silica-alumina has also been noted by others (*15*)], the group of sites on this catalyst cannot be included in the group of sites on any of the impregnated catalysts, even though the latter groups are larger. The difference in the catalytic mechanism may be due to the number of adsorption points associated with each site. A less efficient site may be one aluminum atom, an atom which in some way makes the site "acid," and which distorts the electronic configuration of cumene so that the (net) proton transfer from the propyl group to the ring is facilitated. On the other hand, on the high aluminum catalysts there may be a high incidence of sites involving two adsorption points; with such sites the aromatic ring may be close to the "acid" point and the propyl group may be near some kind of "base" point. Cooperative action between the two sites would result in proton transfer either directly or by way of the two surface points. If the less efficient sites were present, they would not be observed because of the higher activation energy associated with them.

If the active sites of the cogelled catalyst (2.27×10^{14} sites/g) are distributed uniformly over the surface (393 m^2/g), the sites are the order of 10^4 Å apart. While the basis of this calculation is admittedly speculation, the conclusion does cast some doubt on the validity of relating the catalytic activity of these substances to the gross properties of surface aluminum or chemisorbed cumene. It has been suggested by others that active sites constitute a very small fraction of the catalyst surface (*16*).

ACKNOWLEDGMENTS

We are indebted to Mr. J. L. McClanahan, who built the reactor, and to Dr. J. H. Stanton, who made the impregnated catalysts. We appreciate helpful discussion with Professor T. I. Bieber and Mr. R. M. Lago.

REFERENCES

1. THOMAS, C. L., *Ind. Eng. Chem.* **41**, 2564 (1949).
2. HANSFORD, R. C., *ibid.* **39**, 849 (1947).
3. MILLIKEN, T. H., MILLS, G. A., AND OBLAD, A. G., *Discussions Faraday Soc.*, p. 279 (1950).
4. KRAUSE, A., *Ind. Eng. Chem.* **51**, 1358 (1959).
5. HENTZ, R. R., *J. Phys. Chem.* **66**, 1625 (1962).
6. GREENSFELDER, B. S., VOGE, H. H., AND GOODE, G. M., *Ind. Eng. Chem.* **41**, 2573 (1949).

7. Weisz, P. B., and Prater, C. D., *Advan. in Catalysis* **6**, 143 (1954).
8. Prater, C. D., and Lago, R. M., *ibid.* **8**, 298 (1956).
9. (a) Agafonov, A. V., and Kaliko, M. A., *Zhur. Obschei Khim. J. Gen. Chem.* **19**, 39 (1949); (b) Miesserov, K. G., *Izv. Akad. Nauk. SSSR Otdel. Khim. Nauk,* p. 1180 (1956).
10. Maatman, R. W., Lago, R. M., and Prater, C. D., *Advan. in Catalysis* **9**, 531 (1957).
11. Stanton, J., and Maatman, R. W., *J. Colloid Sci.* **18**, 132 (1963).
12. Glasstone, S., Laidler, K., and Eyring, H., "The Theory of Rate Processes," p. 377. McGraw-Hill, New York, 1941.
13. Lago, R. M., private communication.
14. Mills, G. A., Boedecker, E. R., and Oblad, A. G., *J. Am. Chem. Soc.* **72**, 1554 (1950).
15. Nikitina, E. V., and Oborin, V. I., *Izv. Vysshikh. Ucheb. Zavedenii, Neft. i Gaz* (No. 10), p. 75 (1960).
16. Kaliko, M. A., and Pervushina, M. N., *Khim. i Tekhnol. Topliv i Masel* **4** (No. 1), 35 (1959).