JOURNAL OF CATALYSIS 4, 85–89 (1965)

Effects of "Inert" Solids on Heterogeneous Reactions

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Received June 11, 1964

It is shown that high surface area solids when physically mixed with heterogeneous catalysts can exert synergistic effects on hydrocarbon reactions. In particular, pure silica gel of low cracking activity can materially change the apparent activity and selectivity of a regenerated, used silica-alumina cracking catalyst. The implications of these findings for studies of heterogeneous catalysis are explored, particularly as they apply to bifunctional catalysis.

The important observation (*1*) that physical mixtures of two catalysts containing different catalytic functions, e.g., hydrogenation activity and acidity, can be as effective as a single bifunctional catalyst greatly strengthened the twin concepts of mobile intermediates and of catalyst components which interact only through stepwise reactions of these intermediates. These concepts have allowed clarification of a number of complex reaction systems. The purpose of this article is to indicate one of the possible limitations that should be placed on one of these theses, that of catalyst components which interact only via stepwise reactions of mobile reaction intermediates. An example of a second type of interaction between two catalyst components is used as an illustration.

METHODS

Reagents

Feed for the cracking experiments was a West Texas heavy gas oil with the following properties: API gravity, 28.5°; ASTM distillation, °C—IBP, 224°; 10%, 227°; 50%, 353°; 64.5%, 371°; elemental analysis, wt %—C, 85.97; H, 12.80; N, 0.082; S, 1.24; O, 0.18.

The silica-alumina catalyst was "equilibrium" catalyst withdrawn from a commercial fluid catalytic cracker. After the coke on it was burned off, it had the following properties: specific surface, 100 m^2/g; pore volume, 0.268 cc/g; elemental analysis, wt %—Al_2O_3, 12.0; Fe, 0.140; V, 0.0160; Cu, 0.0020; Ni, 0.0113; Cr, 0.0030; Na, 0.080; SiO_2, 88.

Davison grade 950 silica gel was used. It had the following properties: specific surface, 750 m^2/g; pore volume, 0.38 cc/g; elemental analysis, wt %—Al_2O_3, 0.009; Fe, 0.006; Ti, 0.024; Zr, 0.007; Cl, 0.04; SiO_2, 99.9.

Before use it was sieved to remove material held on a 100-mesh screen.

Procedure and Equipment

Cracking experiments were carried out at 500°C in a baffled fluidized fixed-bed reactor at atmospheric pressure. Oil was fed by a metering pump along with sufficient helium to give 51 mole % He at the inlet. Addition of the helium promoted good fluidization of the 400-g catalyst charge which was necessary for good temperature control. Variation in the helium concentration over the range 40 to 60 mole % did not affect catalyst selectivity, nor did it affect activity when correction was made for the difference in contact time. Process periods of 15 min were followed by a 10-min purge with He at 1070 cc/min (STP). Effluent from this purge was combined with the rest of the product for

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distillation (from which the amount of gasoline formed was determined). Gases were analyzed by mass spectrometry. Following the above purge, the reactor was flushed with nitrogen for 30 min at 1000 cc/min before air regeneration of the entire catalyst charge was begun. Separate experiments showed this combination of He purging and nitrogen flushing gave very efficient removal of adsorbed hydrocarbons, i.e., further purging did not remove significant amounts of hydrocarbons. Hydrogen and carbon in the coke were determined as water and carbon dioxide (after oxidation of the carbon monoxide over copper oxide). Product recoveries were between 98 and 102 wt %.

Calculations

Product distributions were calculated from the gas analyses, distillations of the liquid products, and analyses of the regeneration gas. Conversion was defined as 100 minus the weight per cent of products boiling above 221°C. Activities were compared via the space velocities necessary to achieve a particular conversion. In general the product distributions and conversions obtained at three or four space velocities in the range 0.5 to 3.0 were plotted against each other and the product distribution at intermediate conversion read from the smooth curves drawn through the points. In a similar way, the space velocity required for a given conversion was obtained from a smooth curve. A short extrapolation was necessary to obtain the space velocity required for 55% conversion over pure silica gel, since its activity was too low to permit direct measurement in this apparatus. At the low space velocity which would be necessary, gas velocity is too low to assure good fluidization. This extrapolation was made on the reasonable assumption that a plot of conversion vs the logarithm of space velocity has the same slope for silica gel as for silica-alumina.

RESULTS AND DISCUSSION

The elegant work referred to above (*1*) has encouraged other investigators in the field of heterogeneous catalysis to rationalize their results in terms of mobile intermediates and of noninteracting catalyst functions. This investigation deals with a system in which an "inert" component of the catalyst produces synergism and the consequences of such a finding for interpretation of experimental results. To begin, we shall consider three questions: How can the synergistic effects we have observed best be described? What causes them? Under what conditions may we expect to observe them?

Let us deal with the descriptive aspects first. A West Texas heavy gas oil was cracked over a silica-alumina cracking catalyst, pure silica gel, and physical mixtures of these two components. The silica gel was a much less active catalyst on a weight basis (Table 1) and the difference in activity is even greater if the two materials are compared on a surface basis, since the specific surface of the silica was more than 7 times that fo the silica-alumina.

TABLE 1
CRACKING WEST TEXAS HEAVY GAS OIL OVER SILICA GEL AND SILICA-ALUMINA[a]

Catalyst type	Silica-alumina	Silica gel
WHSV	1.64	0.80
Conversion, wt %	48.6	44.0
Products, wt % on feed (no-loss basis)		
H_2	0.21	0.12
CH_4	0.79	1.58
C_2H_4	0.51	1.75
C_2H_6	0.62	2.13
C_3H_6	3.70	2.62
C_3H_8	0.68	1.99
C_4H_8	5.37	1.93
i-C_4H_{10}	1.58	0.12
n-C_4H_{10}	0.45	0.87
C_5-221°C	32.4	28.8
Coke	2.29	2.17
Properties of C_6-221°C gasoline		
Octane number, F-1-O	96	81
Saturates, % vol	24	20
Olefins, % vol	41	59
Aromatics, % vol	35	21

[a] Temperature: 500°C; fluidized fixed-bed reactor; 15-min process period.

The products obtained from the mixtures of silica and silica-alumina (Table 2) are very much like those from silica-alumina alone and are typical of products from

TABLE 2

CRACKING WEST TEXAS HEAVY GAS OIL[a]

Catalyst, wt %				
SiO_2/Al_2O_3	100	75	60	40
SiO_2	0	25	40	60
Relative activity	100	96	95	81
Products, wt % on feed (no-loss basis)				
H_2	0.23	0.26	0.22	0.16
CH_4	1.11	1.31	1.22	1.19
C_2H_4	0.73	0.82	0.85	1.04
C_2H_6	0.80	1.03	1.00	1.12
C_3H_6	5.16	5.28	5.20	4.81
C_3H_8	1.27	1.31	1.22	1.10
C_4H_8	5.90	6.30	5.96	6.10
i-C_4H_{10}	2.71	2.43	2.00	1.36
n-C_4H_{10}	0.63	0.57	0.49	0.57
C_5-221°C	32.60	32.01	33.46	34.76
Coke	3.87	3.67	3.37	2.78
Total	55.01	54.99	54.99	54.99
Properties of C_6-221°C gasoline				
Octane number, F-1-0	96	94	(93)	90
Octane number, F-1-3	(100)	100	99	98
Saturates, % vol	25	20	19	20
Olefins, % vol	33	38	43	47
Aromatics, % vol	41	42	38	33

[a] Temperature: 500°C; 15-min process period; fluidized fixed-bed reactor; 55 wt % conversion.

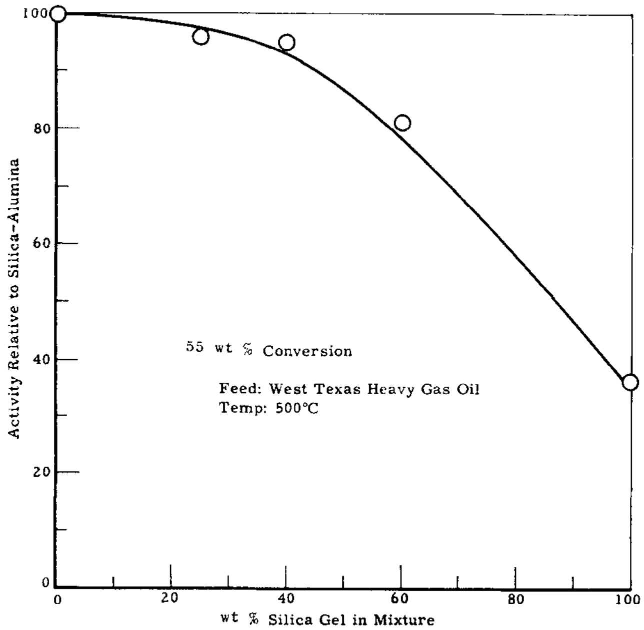

FIG 1. Activity relative to silica-alumina.

carbonium ion cracking (*2*). On the other hand, they differ markedly from those obtained from silica. Specifically, methane, ethane, and ethylene yields are low, while propylene and butylene yields are high. Moreover, the iso/*n*-butane ratios are characteristically high. Surprisingly, the activity of the catalyst mixture does not seem to depend on the concentration of the more active cracking component, silica-alumina, as long as the mixture contains more than 60% silica-alumina (Fig. 1). A brief description of the effect of replacing up to 40% of the silica-alumina with silica is that there is almost no change in the product distribution or the activity of the catalyst. In effect, the silica-alumina remaining in the mixture is more active than in the absence of silica gel.

What can cause this apparent synergism? The feed to these experiments contained many inhibitors (*2*, *3*) of acid-catalyzed cracking, e.g., nitrogen bases and polyaromatics. If these materials are adsorbed on a cracking catalyst they will rapidly condense to form coke (*4*). On the other hand, on a neutral surface such as silica gel, adsorption may only slowly lead to further reaction, i.e., to coke formation and loss of catalytic activity (*4*).* If one retards this coke formation on the silica-alumina, the average activity during the process period should be increased. Let us, then, re-examine the product distributions for the physical mixtures. One effect of substituting silica gel for silica-alumina *is* to be seen: a reduction in coke. The detailed mechanism by which this reduction in coke occurs deserves further consideration. How does an inhibitor adsorbed on a neutral silica surface avoid being burned in the regeneration step (see Procedure and Equipment) and measured as coke? The answer lies in the very efficient stripping provided. Inhibitors which are not polymerized and condensed to coke are removed during this stripping period; the very low partial pressure of inhibitors at this time compared to that during the reaction period when they are initially adsorbed allows them to pass out of the system in the vapor phase. By the above reasoning, and from the data of Blanding (*5*), for example, the activity of the silica-alumina component should increase, perhaps enough to compensate for the higher effective space velocity. Just this is observed. An alternative explanation of the synergisms observed in this system might be based on the lower bulk density of the silica gel compared to the silica-alumina, which results in a somewhat longer catalyst bed. Unpublished experiments with varying bed lengths indicate that this effect is much too small to explain the observations. Moreover, when silica of similar bulk density but lower specific surface was added to silica-alumina, the above effects were not observed.

The third question to be asked is whether the effects seen here are specific for this system or whether they have more general application. The necessary attributes of the two components of the physical mixture seem to be a reactive component whose activity may be inhibited and a second component with the ability to prevent the inhibition. This class is very broad indeed, since it includes not only reactions of compounds containing inhibitors as impurities, but also reactions which are inhibited by products, by products of side reactions, and by products which are in equilibrium with intermediates or with the products. Moreover, the inhibition may be reduced by decomposition of the inhibitors as well as by mere adsorption. For example, it has recently been suggested (*6*) that the kinetics of ethylene hydrogenation over Pt/SiO_2 mixed with alumina show a cooperative effect of the components and that migration of "active hydrogen" from Pt/SiO_2 to alumina is responsible. Effects of the type described above would seem to offer an alternate explanation, since highly unsaturated species are known to be formed from hydrocarbons over platinum catalysts (*7*). Indeed, these species may be responsible for inhibiting the reaction of hydrocarbons over Pt/Al_2O_3 reforming catalysts (*7*).

ACKNOWLEDGMENTS

The authors wish to express their gratitude to Dr. George Holzman for his helpful encouragement,

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* Coke is formed on the silica gel in these mixtures, but only at the lower rate characteristic of pure silica gel.

to Dr. C. P. Brewer for his constructive criticism, and to L. F. Focha for careful experimental help

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