

Assessment of Diffusional Inhibition via Primary and Secondary Cracking Analysis

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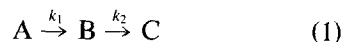
Although the importance of diffusional effects in heterogeneous catalysis has long been recognized, in routine practice this factor is often overlooked. In multicatalyst studies one is prone to attribute differences in activity, selectivity, or activity maintenance to variations in the number and/or kind of active sites. Yet such differences can just as well reflect diffusional factors and failure to realize this can lead to erroneous conclusions. Although diffusional inhibition can occur with any catalyst, the problem is particularly acute with zeolites, in which channel-blocking is a common occurrence. The use of binders and/or high extruding pressures is another factor frequently associated with diffusional restraints.

Methods of evaluating intraparticle diffusional inhibition usually involve the testing of two or more particle sizes of the same material. This procedure can reveal diffusional inhibition only if it exists in the macropores, but not if in the micropores, the lengths of which are unchanged by such manipulation. In addition, this procedure entails duplicate (at least) tests with each catalyst, making it impractical when large numbers of catalysts must be evaluated.

An alternative is to take a kinetic approach. The objective of this paper is to show how cracking, which is a ubiquitous reaction in hydrocarbon catalysis, can be analyzed to obtain diffusional information.

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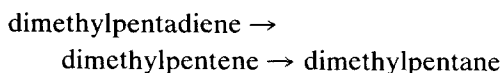
To do this, cracking must be interpreted as a *sequential* reaction, i.e., of the form



The idea of extracting diffusional information from such a reaction is not new. Weisz and Swegler (1), more than 30 years ago, showed that the sequential conversion



catalyzed by chromia-alumina, exhibited a particle-size-dependent selectivity due to diffusional inhibition. Ciola and Burwell (2) made similar observations for the sequence



catalyzed by nickel-silica.

The motivation behind PASCA (primary and secondary cracking analysis) was the desire to exploit the inherent advantages of an *in situ* sequential reaction. Consider, e.g., a group of catalysts being studied for aromatization. Cracking inevitably occurs as a side reaction, and, if properly interpreted, could provide diffusional information without the need for additional experiments. Furthermore, since this information is generated *in situ*, it will automatically be identified with the exact experimental conditions and state-of-catalyst (degree of coke deposition, sintering, etc.) that correspond to the aromatization data.

We will first describe the mechanics of PASCA, showing how sequential reaction analysis is possible despite the lack of a formal "B" and "C" molecule. Based on this,

an index of diffusional inhibition will be derived. Finally, experimental data illustrating the application of PASCA will be presented.

RESOLVING THE CRACKING PATTERN INTO ITS PRIMARY AND SECONDARY COMPONENTS

When a molecule cracks, the daughter molecules may crack again. This has the essence of a sequential reaction, with *primary* cracking represented by $A \rightarrow B$ and *secondary* cracking (cracking of the daughter molecules) by $B \rightarrow C$.

We illustrate PASCA for the case of a C_6 -paraffin feed. Primary cracking is defined, for this system, as the cracking of hexane (*n*- or iso-) to give lighter molecules, denoted collectively as C_{1-5} , i.e., molecules with a carbon number less than 6. Secondary cracking refers to the scission of the daughter molecules (ethane, propane, butane, or pentane), denoted collectively as C_{2-5} .

The amount of primary cracking is simply the number of moles of hexane that have cracked. Let A_{PC} denote the amount that has occurred within a unit volume of gas exiting from the catalyst. Similarly, the amount of secondary cracking is the number of moles of C_{2-5} that have cracked; let A_{SC} indicate this quantity for the same unit volume.

Primary and secondary cracking have different effects on the number of moles of C_{1-5} (denoted by $n_{C_{1-5}}$) and on the number of carbon atoms contained in these moles (denoted by $a_{C_{1-5}}$). Cracking a mole of hexane increases $n_{C_{1-5}}$ by two and $a_{C_{1-5}}$ by six. Cracking a mole of C_{2-5} increases $n_{C_{1-5}}$ by one but has no effect on $a_{C_{1-5}}$. Defining μ as the size of the average C_{1-5} molecule, i.e.,

$$\mu = a_{C_{1-5}}/n_{C_{1-5}} = \sum_{i=1}^5 i n_{C_i} / \sum_{i=1}^5 n_{C_i}, \quad (2)$$

where n_{C_i} denotes the number of moles of molecules containing i carbon atoms, it is seen that for purely primary cracking, $\mu = 3$.

To determine A_{PC} , it is necessary only to know the total number of carbon atoms contained in the C_{1-5} molecules, irrespective of the number of moles these are distributed among. Since, as noted above, hexane cracking adds six to $a_{C_{1-5}}$, we have

$$A_{PC} = a_{C_{1-5}}/6, \quad (3)$$

which, using Eq. (2), gives

$$A_{PC} = n_{C_{1-5}}(\mu/6). \quad (4)$$

As previously stated cracking a mole of ethane, propane, butane, or pentane increases $n_{C_{1-5}}$ by one while leaving $a_{C_{1-5}}$ unchanged. To evaluate A_{SC} we start with $n_{C_{1-5}}$ and subtract the amount of $n_{C_{1-5}}$ attributable to primary cracking. Since the latter is equal to $a_{C_{1-5}}/3$, we have

$$A_{SC} = n_{C_{1-5}} - a_{C_{1-5}}/3, \quad (5)$$

which, using Eq. (2), becomes

$$A_{SC} = n_{C_{1-5}}[(3 - \mu)/3]. \quad (6)$$

Thus, primary and secondary cracking can be resolved by determining (i) the total number of moles of C_{1-5} molecules and (ii) the average size (i.e., number of carbon atoms) of these molecules. The ratio of secondary to primary cracking emerges as a single-valued function of μ :

$$A_{SC}/A_{PC} = 2(3 - \mu)/\mu. \quad (7)$$

Equation (7) reduces to zero in the absence of secondary cracking since, as previously noted, $\mu = 3$ in this case. For complete degradation to methane ($\mu = 1$), $A_{SC}/A_{PC} = 4$, since four scissions of C_{2-5} molecules are required.

USING PASCA TO OBTAIN AN INDEX OF DIFFUSIONAL INHIBITION

The selectivity of a sequential reaction, i.e., the ratio of B/C in the product, is known to be influenced by diffusional inhibition in the catalyst. Mathematical descriptions have been given by Weisz and Swegler (1) and by Peterson (3). These effects can be understood with reference to the concentration of the intermediate spe-

cies, B. In the absence of diffusional inhibition the fluid phase value B_0 will be identical to the average concentration of B inside the catalyst particle \bar{B} . Diffusional inhibition creates an intraparticle gradient, with $\bar{B} > B_0$ (we are assuming that the reaction $B \rightarrow C$ is small compared to $A \rightarrow B$). This can be pictured as the rate of formation of B being large relative to the ability of the pores to convey B molecules out of the particle, so that an overconcentration develops.

Since catalytic rates depend on intraparticle concentrations, the inequality $\bar{B} > B_0$ is reflected in a greater rate of formation of C, with the ratio C/B increasing along with \bar{B}/B_0 . Assuming quasidifferential conversions, C/B is a convenient index which provides, on a relative basis, the degrees of diffusional inhibition of various catalysts being compared under similar conditions.

PASCA, of course, has no "B" molecule and no "C" molecule. These are defined functionally. Each scission of a C_{2-5} molecule leads to a net increase of one molecule of C_{1-5} . These "additional" moles, counted by Eq. (6), constitute the final product "C." The corresponding reactant "B" is the C_{2-5} that cracks to produce the "additional" moles. (Note that *hexane* cracking does *not* produce "additional" moles; since $n_{C_{1-5}}$ increases by two and $a_{C_{1-5}}$ by six, the net effect on Eq. (5) is zero.) To an extent, "B" is not annihilated by secondary cracking since, e.g., the products of the reaction



can crack (this subsequent cracking is generically referred to as secondary cracking) to generate more "additional" moles. "B" is not inexhaustible, however, since each C_{2-5} scission reduces (by 1) the number of carbon-carbon bonds available for subsequent cracking.

If we assume that the ratio of secondary to primary cracking is small, the concentration of C_{2-5} ("B") will essentially equal twice the number of moles of hexane that have cracked, i.e., $2A_{PC}$; using Eq. (4), we obtain

$$B = 2A_{PC} = n_{C_{1-5}}(\mu/3). \quad (8)$$

"C" has been defined as the "additional" moles resulting from secondary cracking; therefore,

$$C = A_{SC} = n_{C_{1-5}}[(3 - \mu)/3]. \quad (9)$$

Thus, the index of diffusional inhibition is given by

$$C/B = A_{SC}/2A_{PC} = (3 - \mu)/\mu. \quad (10)$$

Equation (10) indicates that a comparison of the diffusional inhibitions among several catalysts can be obtained directly from their A_{SC}/A_{PC} ratios.

EXPERIMENTAL APPLICATION OF PASCA

To demonstrate the application of PASCA we have studied the effect of particle size on the cracking patterns of Pt, Ir/alumina catalysts used for the reforming of 3 methylpentane (3MP). If macropore diffusional inhibition exists, larger particles should exhibit higher A_{SC}/A_{PC} ratios. The catalysts were prepared by impregnating γ -alumina (190 m²/g) with an aqueous solution containing H_2PtCl_6 , H_2IrCl_6 , and HCl. The impregnates were dried 16 h at 110°C and air-calcined 16 h at 250°C. Total metal loadings were either 0.2% Pt-0.2% Ir or 0.3% Pt-0.3% Ir. All catalysts contained 1.2 wt% total chloride.

3MP reforming was carried out at 100-psig pressure with a $H_2/3MP$ mole ratio of six. The catalyst charge was 50-200 mg, which was mixed with 2-g quartz particles and loaded into a fixed-bed, stainless-steel, downflow reactor. It was dried *in situ* with He at 600 cc/min at 120°C for 2 h and then reduced with H_2 at 285 cc/min at 350°C for 45 min followed by 30 min at 525°C. The temperature was then reduced to 450°C whereupon liquid feed commenced at 15.4 cc/h. Temperature was then increased to 510°C and data collection begun.

Effluent from the reactor was conducted through heated lines to a HP 5880A gas chromatograph equipped with a flame ionization detector and a SP 2100 column for

on-line analysis. Column temperature was programed from 40 to 250°C over 30 min and then held at 250°C for 30 min. This allowed the elution of peaks through C₁₀ although combined post-toluene peaks were <0.2%.

The effect of particle size on the PASCA parameters of a 0.2% Pt, 0.2% Ir/alumina catalyst is shown in Table 1. The powdered catalyst was pressed into a wafer which was broken and sieved to provide 12/20 and 80/120 mesh fractions. These were run at a space velocity of 50 wt/wt/h. Data was recorded after 12- to 14-h exposure to feed at 510°C and after a subsequent drop to 430°C.

Table 1 lists the product distributions and the values of some PASCA-related parameters. For convenience, we have chosen the unit of volume to be that which contains 100 g of hydrocarbon. Although not strictly constant, the discrepancy is small for high H₂/hydrocarbon ratios, as used here. Thus, for the first column in Table 1, $n_{C_1} = 7.78/MW_{(CH_4)}$, $n_{C_2} = 5.66/MW_{(C_2H_6)}$, etc. Values

of μ , A_{PC} , and A_{SC} are obtained from Eqs. (2), (4), and (6), respectively. As previously mentioned, 3MP is lumped with its isomerization products 2MP and nC_6 to define the primary reactant for cracking. Since the three isomers have similar cracking rates this will have little effect on PASCA even if two catalysts with very different isomerization rates are compared.

Turning to the 510°C data, there is a clear effect of particle size on the cracking pattern. The average C₁₋₅ molecule produced by the 80/120 mesh particles contains 2.44 carbon atoms, but with 12/20 mesh particles this is reduced to 2.18 carbon atoms. Rates of primary cracking agree to within 5%, but 74% more secondary cracking is observed with the larger particles.

On lowering the temperature to 430°C, A_{SC}/A_{PC} decreases for both particle sizes. This is expected, since a lower reaction rate reduces diffusional inhibition. There is still, however, a significant difference in A_{SC}/A_{PC} between large and small particles.

TABLE 1
Effect of Particle Size on 3MP Reforming over 0.2% Pt-0.2% Ir/Al₂O₃

Wt%	510°C		430°C	
	Particle size		Particle size	
	12/20 Mesh (1.68/0.84 mm)	80/120 Mesh (0.177/0.149 mm)	12/20 Mesh (1.68/0.841 mm)	80/120 Mesh (0.177/0.149 mm)
C ₁	7.78	5.23	1.16	0.95
C ₂	5.66	5.28	1.09	0.90
C ₃	4.48	4.48	0.66	0.58
<i>i</i> -C ₄	2.91	3.16	0.58	0.51
<i>n</i> -C ₄	4.00	4.15	1.06	1.02
<i>i</i> -C ₅	4.50	4.83	2.52	2.37
<i>n</i> -C ₅	3.27	3.46	0.77	0.76
2MP	18.08	25.67	13.79	18.40
3MP	34.68	24.63	74.76	69.57
<i>n</i> C ₆	7.82	11.08	2.50	3.39
Methylcyclopentane	1.43	1.93	0.90	1.17
Benzene	5.00	5.68	0.26	0.37
Toulene	0.28	0.26	0.01	0.01
$n_{C_{1-5}}$	1.004	0.846	0.198	0.173
μ	2.177	2.440	2.689	2.793
A_{PC}	0.364	0.344	0.089	0.0805
A_{SC}	0.275	0.158	0.0205	0.0119
A_{SC}/A_{PC}	0.756	0.459	0.230	0.148

Six other comparisons of large-particle (12/20 mesh) and small-particle (60/80 mesh) catalysts were made, with results similar to those just described. Space velocity varied from 50–200 wt/wt/h and the temperature was 510°C. Comparisons were always made with particles from the same pressed wafer, in order to eliminate batch-to-batch pilling variations, which were significant. A lower value of A_{SC}/A_{PC} was always obtained with smaller particles; in most cases this effect was greater than shown in Table 1.

The influence of diffusional inhibition of some specific irreversible reactions can be seen in Table 1. Primary cracking shows no effect, with A_{PC} 5% lower (at 510°C) for the smaller particles, which is within the run-to-run variability. The smaller particles, however, produce 14% more benzene. This modest influence of diffusional inhibition is roughly in agreement with a calculation of the Weisz criterion (4)

$$\frac{R^2}{D_{EFF}} \left(-\frac{1}{Vc} \frac{dn}{dt} \right) \frac{1}{C_s}$$

for the larger particles, where R is the particle radius, D_{EFF} the effective Knudsen diffusivity of 3MP, $(-1/Vc) dn/dt$ the reaction rate (cracking plus aromatization) per unit volume of catalyst, and C_s the reactant concentration. With an estimated D_{EFF} of 6.9×10^{-3} cm²/s, we calculated a value of 2.6 for the Weisz criterion. This corresponds to an effectiveness factor (4) of 88%. The much larger effect of particle size on A_{SC}/A_{PC} illustrates the sensitivity of PASCA. This is due to the fact that PASCA is based on the intraparticle concentration gradient of the product molecule, whereas the effectiveness factor reflects the gradient of the feed molecule. For low to moderate conversions the relative effect of the intraparticle gradient will be much greater for the product molecule.

The fact that large-particle Pt,Ir/alumina exhibits a greater A_{SC}/A_{PC} ratio than smaller particles of the same material

points clearly to diffusional inhibition which is aggravated by increased particle size. As pointed out above, such particle-size dependency points to *macropore*-diffusion inhibition (perhaps coexisting with a micropore component) and affords a simple illustration of PASCA. However, since *any* cracked-product concentration gradient (macropore or micropore) will affect PASCA, the latter will be helpful in situations where particle-size variation is not; zeolite-channel blockage is one example of this.

It may be mentioned that the triangulation method of estimating diffusional resistance, used in Ref. (1), requires, in general, knowledge of the individual rate constants k_1 and k_2 ; an exception is the limit of strong diffusional inhibition, in which case only the ratio k_2/k_1 is needed. PASCA, when applied under conditions of quasi-differential conversions, requires only that k_2/k_1 be reasonably constant across the data base. In most cases this will be fulfilled, since catalysts having higher cracking activities for hexane will have commensurately higher activities for propane, butane, etc. However, acid-cracking catalysts can be expected to have lower k_2/k_1 ratios than metal-cracking catalysts, due to the instability of primary carbonium ions, which affects the cracking of lighter molecules more than that of heavier ones. Therefore if these two types of catalysts are compared, a correction for the difference in the k_2/k_1 ratio should be applied. It should also be noted that PASCA is probably not applicable to metals such as iron due to surface retention of cracked products which leads almost exclusively to methane.

In conclusion, we believe PASCA to be an effective *in situ* technique that affords a new approach to the often overlooked problem of estimating diffusional inhibition.

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