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CATALYST POISONING

Empirical Relationships: Poisoning of Silica-alumina with Organic Bases

By

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Abstract

The types of deactivation of solid catalysts, and the more common forms used for relating them empirically, are briefly reviewed. The decrease in activity of an acid catalyst (silica-alumina) to dehydrate methanol at 228°C, by the successive addition of organic bases, is studied. The poisoning action of the different substances decreases as follows: dimethylaniline, diethylamine, pyrrole, piperidine, and pyridine. It was found that activity falls linearly for the first portions of poison (homogeneity of the active sites) and that toxicity depends on chemisorption (basicity), thermal stability and physical adsorption (boiling point or polymerization capacity). The amount of base needed to deactivate the catalyst is much less than the acidity determined by the *n*-butylamine method.

The usefulness of a catalyst for an industrial process depends on its activity, selectivity and its stability. Activity is the catalyst's capacity to accelerate the transformation from reactants to products. Selectivity is the relation between the desired and the undesired products. Stability is the property of conserving activity and selectivity during operation while all parameters remain constants.

In many processes with solid catalysts production decreases more or less rapidly. This loss of activity of the catalyst may be due to the deposition of carbonaceous material (fouling), the adsorption of poisons, or the modification of its physical structure (aging). Aging is irreversible: it is due to changes in the physical structure of the catalyst. It is very influenced upon by temperature and little by the reactants present. Instead, poisoning and fouling are produced by the substances present. Poisoning is caused by substances that adsorb more strongly than the reactants, either in a reversible or irreversible way. In the first case, when the poison disappears from the stream of reactants it desorbs from the catalyst surface, which regains its activity. The carbonaceous deposit is formed from unsaturated hydrocarbons

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(olefins, aromatics) or other easily polymerized products.

The more common solid catalysts are metals (mainly those which belong to group VIII of the Periodic Table), oxides (insulating or semiconductors), sulfides and halides. The most sensible to poisons are the metals of group VIII (transition) and the insulating oxides.

The present work refers mainly to poisoning by chemisorption. The empirical expressions that can be used to relate catalytic deactivation are quoted, and results are given of studies on poisoning by organic bases of silica-alumina used in the dehydration of methanol.

Empirical relationships

If the activity (kinetic constant, conversion of reactants to products, or amount obtained of a certain substance) is called A , and the amount of that which causes deactivation (carbonaceous deposit or adsorbed poison) is called C , a plot of A as a function of C is generally a curve which shows a rapid decrease of A for the first portions of C . Slope decrease as the amount of C increases. This indicates that the "deactivation rate" of the catalyst, dA/dC , decreases with C . To find how A and C are related, the equations indicated in Table 1 are charted. The plot which best approximates a straight line shows the most convenient expression.

TABLE 1

Type of equation	Plot in which it gives a straight line	Deactivation rate dA/dC
I) $A = A_0 - bC$	A vs. C	$-b$
II) $A = A_0 10^{-bC}$	$\log A$ vs. C	$-2.3 bA$
III) $A = a - b \log C$	A vs. $\log C$	$-b/2.3 C$
IV) $A = aC^{-b}$	$\log A$ vs. $\log C$	$-b A/C$

A_0 is the initial activity, and the letters a and b are positive constants which can be determined with the slope and a point of the straight line. The coefficient b characterizes deactivation: the rate of decrement of A is always proportional to b . In all the equations A approximates zero when C is very high; only the straight line and the exponential have a finite value for $C=0$, and when C is small both take similar values. For the other equations A is infinite at $C=0$, and when C starts increasing they show a sudden fall of A .

Fig. 1 shows the curves that correspond to the equations of Table 1, calculated with two known points. Types I and II have been found useful

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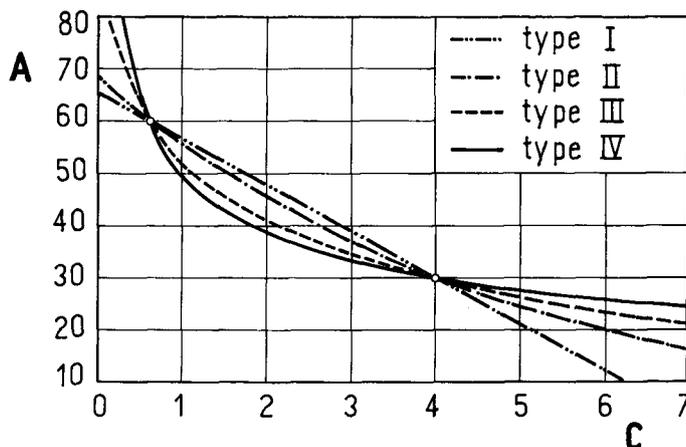


Fig. 1. Curves corresponding to the types of equation indicated in Table 1, with the following data: $A=60$ when $C=0.6$, and $A=30$ when $C=4$.

in poisoning, where A_0 and the values of A are measured by adding successive amounts of C . Type I indicates that all the active sites have the same activity. Types III and IV usually represent the data of a very strong deactivation, such as fouling due to carbonaceous deposit formed from reactants, where it is impossible to determine A .

Poisoning of metallic catalysts

The catalytic activity of transition metals is attributed to the vacant places in their orbitals, which are filled in by the electrons of the reacting molecules. In this way they bind to the catalyst. Therefore, when an undesired or strange body is adsorbed in these sites, catalyst activity decreases. Among the poisons of these metals are those substances that contain elements from groups Vb and VIb, which are not completely saturated, and the compounds with multiple bonds, such as carbon monoxide. MAXTED,¹⁾ in his complete work, indicates how the poisoning action can be eliminated from these substances by transforming them (by oxidation or hydrogenation) into saturated compounds. In several liquid phase reactions, in static systems and with platinum, palladium or nickel as catalysts, he found that, on plotting activity as a function of the amount of poison added, a linear decrease is obtained as the amount of poison increases. This action persists until activity falls to a value of approximately one third of initial activity. At this point the curve presents an inflection, and from there onwards it has an ever decreasing slope, showing that fall of activity is slower each time. That is to say that a great part of

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the curve obeys a type I equation :

$$A = A_0 - bC = A_0(1 - \alpha C). \quad (1)$$

The poisoning coefficient, α , is used to compare the toxic action of different substances. This coefficient is the reciprocal of the amount of poison theoretically needed to totally inhibit activity if the decrease were linear up to the end. MAXTED shows that, for a series of substances with the same toxic atom, α increases with the molecular weight. This could have an explanation in the greater "covering" of the catalytic surface produced by the big molecules, which would cover several adjacent active sites. Therefore, for small amounts of poison, the fall of activity would be proportional to those amounts. But after a certain degree of covering has taken place there are less and less active sites suitable for the adsorption of the poison. Based on the form of the adsorption isotherm, GERMAIN²⁾ indicated that the linear fall is associated with a strong adsorption of the poison, while a weak adsorption would give an exponential decrease.

Many papers on the subject indicate that there is a stronger activity fall with the first portions of the poison and that the corresponding curve does not follow a straight line. According to the different cases one of the other empirical equations can best represent the data.

KARN *et al.*^{3,4)} studied the poisoning with hydrogen sulphide of the iron catalyst used in the Fischer-Tropsch reaction. They found that the activity fall in some cases followed an exponential curve, in others a hyperbole or a straight line. TEICHERT and CIBOROWSKY⁵⁾ studied the poisoning by hydrogen sulphide of several nickel catalysts used in the hydrogenation of benzene, and interpreted the activity fall with an exponential type expression.

Poisoning of insulating oxide catalysts

The insulating oxide catalysts are very important for their use in many reactions of the petroleum industry. Their catalytic activity is attributed to the presence of acid sites on their surface. This indicates that the neutralizing of acidity would give place to a poisoning of the catalyst. Particularly important is the poisoning of silica-alumina used in the cracking of hydrocarbons, which is sensible to the nitrogen organic bases present in petroleum and to alkaline metals.

MILLS, BOEDEKER and OBLAD⁶⁾ found that the addition of organic bases produced an exponential fall of activity in the cracking of isopropyl benzene. This would show that there is no uniformity in the activity of the active centers and that the stronger ones suffer poisoning first. They also found

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that the poisoning action depends not only on the basicity but also on the volatility of the base employed. The poisoning action is caused by a combined effect of chemisorption and VAN DER WAALS attraction forces (volatility of the base used). The same thing was shown by VOGEL, GOOD and GREENSFELDER⁷⁾: ammonia and aliphatic amines have little inhibiting action in decaline cracking at 500°C., while bases of higher molecular weight are strong poisons.

Other authors⁸⁾ studied the adsorption and poisoning of basic nitrogen compounds on cracking catalysts and found that the amounts adsorbed on the catalysts were approximately proportional to the basicities of the poisons.

TURKEVICH *et al.*⁹⁾ studied the cracking of isopropylbenzene on molecular sieves. By poisoning the catalyst injecting quinoline and tributylamine they found a linear fall of activity with the amount of poison added, and this was used to titrate the surface acidity.

The poisoning action of organic bases can be avoided by eliminating them from the feed, such as in the example given by MUSHENKO and MOCHALOVSKAYA.¹⁰⁾ When they are directly on the catalysts they can be burnt off, for they are combustible substances.

Regarding the poisoning of cracking catalyst with alkaline ions, MIESEROV¹¹⁾ and STRIGHT and DANFORTH¹²⁾ measured the catalytic activity of silica-alumina impregnated with different amounts of alkaline salts and found that the activity falls linearly with alkali content. DANFORTH¹³⁾ found in the silica-alumina poisoned with alkali metal ions, that the poisoning effect of the ion increased with the ion size, similarly to the results obtained with organic bases.

Fouling

Due to the great importance of fouling in petroleum industry several mathematical models have been developed to relate activity to the inactivating carbonaceous deposit. These relations are complicated and even so do not represent the complex phenomena which really occur. Therefore experimental data are usually related in an empirical way.

The curves which indicate the deactivation of silica-alumina by fouling in the cracking of gas-oil present a rapid fall for the first parts of deposit formed, usually giving straight lines in a log-log chart. VOORHIES¹⁴⁾ found that $b=0.43$ in the power expression. Many authors give conversion and amount of carbon deposit as functions of time, obtaining straight lines in a log-log paper. From the curves drawn by WHITAKER and KINZER¹⁵⁾ can be obtained a value of $b=0.50$. From the chart of PRATER and LAGO¹⁶⁾ with data from the cracking of isopropylbenzene, with acetophenone as a deposit forming agent, the value of b is found to be 0.8.

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Poisoning of the Reaction of Dehydration of Methanol over Silica-alumina

Experimental determinations

The dehydration of methanol was carried out in a flow apparatus at 228°C. passing gaseous methanol over silica-alumina. Under these conditions the reaction is selective and only dimethyl ether and water are produced.

The main parts of the laboratory set-up are: liquid methanol feeder, vaporizer, reactor, methanol-water condenser and a device to measure the amount of gas produced (dimethyl ether). The catalyst was Synclyst silica-alumina, 13% Al_2O_3 , provided by J. Crosfield & Sons Ltd. This catalyst was pelleted and powdered, the fraction 50-80 mesh was separated and activated in air at 480°C. Its specific surface area is 460 sq.m/g. The acidity, determined with n-butylamine at room temperature, by the method of JOHNSON,¹⁷⁾ and using anthraquinone as a dye is 0.35 m.eq./g. Methanol and the organic bases were pure grade and were used without further purification.

In each run 8 g of catalyst were used and liquid methanol was fed at a rate of 8 ml/h. Under these conditions the amount of gas produced (A_0) was

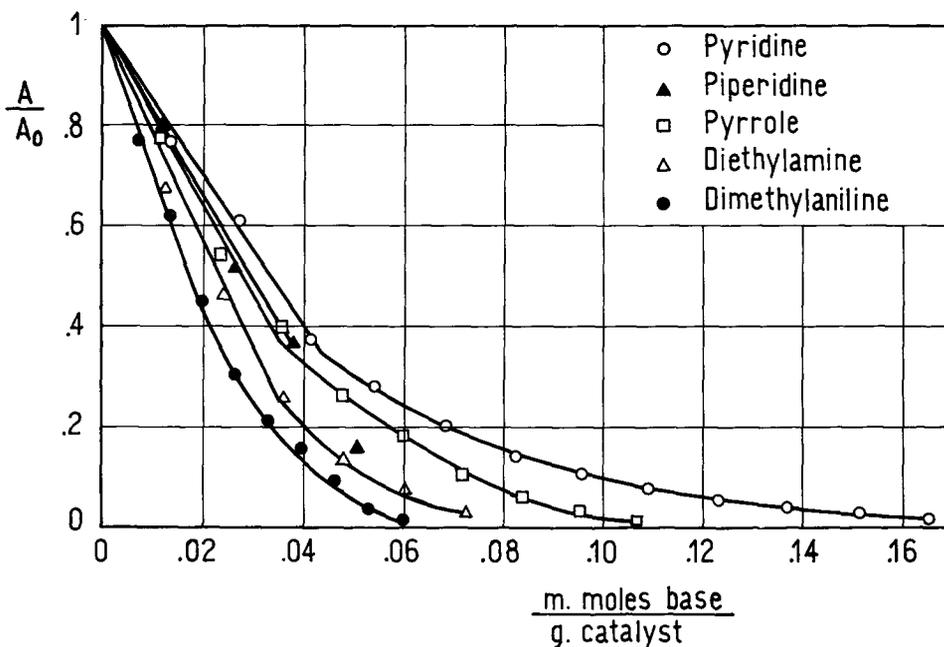


Fig. 2. Activity fall for successive injections of an organic base in the dehydration of methanol over silica-alumina at 228°C.

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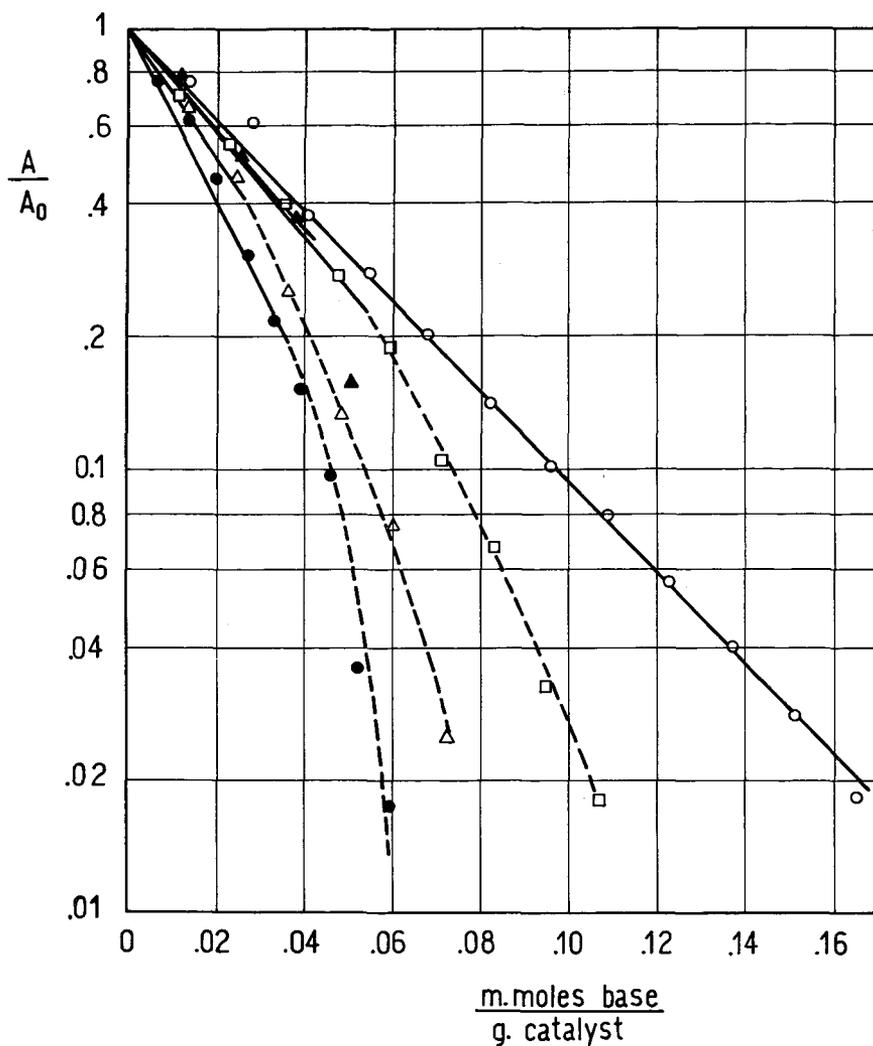


Fig. 3.

870 ml/h., at room temperature and atmospheric pressure. Each run began by feeding methanol and then, maintaining the same flow rate, the bases were added to the vaporizer. This operation was done with a syringe, adding 0.5 or 1 ml each time of a 0.1 M solution of the base in benzene. The variations of the gas flow rate at the outlet were measured, which gave the values of A. Results are shown in an arithmetic plot in Fig. 2 and in a semilog one in Fig. 3.

Discussion of results

Fig. 2 indicates that the activity falls are similar to those obtained by MAXTED¹⁾ with metallic catalysts. The exponential type of fall shown in Fig. 3 is alike that of a similar catalyst used by MILLS, BOEDEKER and OBIAD⁶⁾ in the cracking of isopropylbenzene.

Only the slow activity fall produced by pyridine has nearly all the points on the exponential curve. When the poison is stronger the curve is less like an exponential, presenting a greater slope.

It can be seen in Fig. 1 that for small values of C an exponential fall does not differ much from a linear one. Of the two types of plot, the most convenient is the arithmetic one. Although for several poisons the semilog chart may give a straight line in a wider range of activities, the arithmetic one presents the advantage of having coefficients that can be given a physical meaning. This is obvious from Eq. (1):

$$\alpha = \frac{b}{A_0} = \frac{1}{C_M}, \quad (2)$$

where C_M would be the hypothetical concentration of active sites in the catalyst. This is for a given poison, if the activity fall were linear all the way, and if each molecule of poison covers one active site.

The straight part of the curve indicates that on adding poison, sites of equal activity are cancelled. The part of the curve that follows could indicate the existence of heterogeneity, with weaker acid sites which contribute little to the total activity. More possibly, it could be showing that the bases affect several acid sites on adsorbing, which is what each molecule does independently when the number of them added is small; but towards the end they would neutralize activity in areas where some active sites have already been cancelled.

The curves have a similar shape in the case of poisoning at the pore mouth in cases where there is a limitation of the reaction due to poor diffusion, as was established by WHEELER.¹⁸⁾ But using the WEISZ and PRATER¹⁹⁾ criterion it has been found that a diffusive limitation is not possible under the conditions employed.

In Table 2 are given, for each base, the values of its poisoning capacity, α , as well as other interesting properties. The values of pK were taken from NOLLER²⁰⁾ and correspond to conditions which differ much from the experimental ones. Nevertheless, they will give an idea of the relative basicity of each substance. Boiling points are given as a volatility criterion, for a high boiling point indicates the possibility of a strong influence of van der Waals forces.

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TABLE 2

Substance	α g catalyst m moles base	pK	bp (°C)
Dimethylaniline	28	5.1	193
Diethylamine	21	11.0	56
Pyrrole	18	0.4	131
Piperidine	17	11.2	106
Pyridine	15	5.3	116

To a greater pK there is not a corresponding increase of the poisoning action. Dimethylaniline, although it is less basic than diethylamine, has a greater poisoning capacity. This may be due to its small volatility. Diethylamine has a boiling point which is far below working temperature, and it is adsorbed to a much lesser extent. In this case physical adsorption would be much more important than the basicity of the substance. Pyrrole, in spite of its weak basicity and low boiling point, has the property of polymerizing in the presence of acids,⁶⁾ therefore giving substances of low volatility and great poisoning capacity. There would be a small number of molecules formed, but they would affect many acid sites. Piperidine, although it is very basic, has a small inhibiting action. This anomalous behavior is probably due to its decomposition over the catalyst, as was also quoted before.⁶⁾

The values of C_M are much smaller than the acidity values determined by the n-butylamine method at room temperature, which indicates that only part of total acidity is active. Besides, C_M values are different for each base, this value would be a function of the power of each one to act upon several acid sites at a time.

Under the working conditions already mentioned the amount of pyrrole and piperidine necessary to neutralize the catalyst activity is similar to that needed to inhibit the cracking of isopropylbenzene at 427°C.⁶⁾

Conclusions

In the gas phase dehydration of methanol over silica-alumina a great part of the active sites have equal activity.

The amount of organic base needed to inhibit activity is different for each one. The poisoning action depends on the basicity, and it is very influenced upon by the boiling point of the poison, as well as by its decomposing or polymerizing properties. The amount needed to inhibit activity to a nearly complete extent is much less than that theoretically needed according to acidity

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measurements by the classical method at room temperature. This amount is nearly the same as that used to neutralize activity in a similar catalyst in the cracking of isopropylbenzene.

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