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METHODS FOR ESTIMATION OF CRUDE OIL PROCESSING CATALYST ACTIVITY 1/

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C O N T E N T S

I. Introduction

Due to the fact that the importance of the catalytic processes in the crude oil processing industry is steadily increasing, special attention is being given to research work on catalytic processes and catalysts.

Research regarding the elaboration of new catalytic systems as well as the control of catalyst fabrication and of the life and performance of catalysts during operation, involves a large volume of work for the complex characterization of the catalysts, ample equipment as well as high trained personnel specialized in various fields of chemistry and physics. The main criterion in the estimation and selection of catalysts is their activity and selectivity as well as stability, namely, " life " under operating conditions in the commercial plants.

Determination of activity and selectivity of catalysts in carried out in micro-reactors or other laboratory equipment, pilot plants and even in commercial plants. To date, experiments carried out in commercial plants are the only one by which full information can be obtained regarding the performance of catalysts, which is the most severe test which must be passed by a new catalyst. Pilot units are built so as to reproduce as closely as possible, on a small scale, the parameters of commercial reactors. Testing of catalysts in such units is carried out in conditions very similar to those encountered in commercial plants to obtain experimental results, enabling adaption to a commercial scale. Experiments carried out in commercial plants and pilot units are expensive, requiring large quantities of materials, costly installations, with a high degree of automation and much time.

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It is evident that economical considerations require that the greater part of work related to the characterization of catalyst activity be carried out in the laboratory, while pilot unit experiments should be carried out only with those samples of catalysts previously selected by laboratory tests.

In the following paragraphs, reference shall be made only to work regarding the determination of catalyst activity at laboratory scale. This is due to two reasons :

- the increasing interest of researchers in such work and future possibilities to study catalytic process kinetics and differentiation of catalytic functions in the frequent case of complex catalysts ;

- the existence of standardized and fully experimented procedures, where there is a possibility of interpreting the data in correlation with those obtained commercially with catalysts of the same type.

II. Problems in solid catalyst activity determination

Determination of catalytic activity means the measurement of a certain reaction velocity in presence of the catalyst and the determination of the selectivity for the desired product. Measurement of reaction velocity in a single set of experimental conditions, allows the selection of catalysts, on condition that experimental conditions remains strictly unmodified during the entire experimental cycle. By varying reaction conditions, informations are obtained on the kinetic of the heterogenous catalytic reaction (activation energy, order of reaction, reaction velocity equation), which is especially useful for a more severe selection of the catalytic system and,in some cases, for the design of commer-

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cial catalytic reactors.

It is well known that a reaction, catalysed by a porous solid, comprises a series of mass and heat transfer effects to and from the catalytic surface. Therefore, mass transfers occurs in the following stages :

-transfer of reactant molecules from the fluid stream surrounding the catalyst particles to its outer surface ;

-diffusion of reactant molecules within the catalyst pores ;

-chemisorption of reactant molecules on pore walls ;

-reaction of chemisorbed molecules ;

-desorbtion of reaction products ;

-diffusion of reaction product molecules out of pores ;

-transfer of reaction product molecules from the catalysts outer surface into the fluid stream.

Heat transfer takes place simultaneously, through a series of analog stages, which, for a endothermic reaction, may be sketched as follows :

-heat transfer from the fluid stream to the catalysts outer surface ;

-heat transfer from outer surface of catalyst towards its inside surface ;

-heat absorption during chemical reaction.

The complexity of the phenomena associated with a heterogenous catalysed reaction dictates special care when experimental data obtained in a catalyst reactor are interpreted. The physical phenomena associated with the cata-

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lytic reactions can considerably influence the development of an experiment, and the results obtained may not correctly reflect the activity and selectivity of the catalyst under study. In this sens it is useful to give several examples.

The distribution of the catalysts pore size may have a considerable effect upon the experimental data. In most of the reactions under hydrogen pressure, its function is to avoid formation and accumulation of precursors that would lead to polymeric substances, wich block the catalyst pores and diminish its active surface and implicit the activity. If the hydrogen does not have total access to the inner section of the catalyst, the polymerization and degradation processes of the catalyst activity may occur in the inner part of the catalyst particles. In such a case the catalyst appears to have a low activity although the nature of its surface is adequate for obtaining high conversion degrees, in fact the catalyst has a high activity concealed by the parasitical phenomena that can be developed due to obsturuction of diffusion within the pores.

The temperature inside the reactor is measured in the reactant stream. In the case of reactions with high thermal effects, the temperature at the surface of the catalyst may differ greatly from that measured and can lead to wrong conclusions.

In view of the above, experiments in laboratory units should be carried out in such a manner as to be influenced as little as possible by mass and heat transfer phenomena. As a rule, this could be achieved by :

- creating a high turbulence in the fluid stream ;
- using small particles of catalyst, with large sized pores and high thermal conductivity ;

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-choosing such operating conditions that low conversions would be obtained (below 10 %), far away from the thermodynamic equilibrium corresponding to the reactor temperature.

If the above conditions are achieved, the reactor shall operate practically under izothermal conditions, while the partial reactant pressures, before and after the catalyst layer, will be practically equal. A reactor which operates under these conditions is called differential.

Most of the laboratory reactors with which have been working for several years, are different from the differential ones, the so called integral reactor being used. Such reactors, with a fixed bed catalyst, obtain high conversions, similar to commercial ones and information is quickly obtained regarding the possibility to applya certain catalytic system in the industry. With such reactors it is difficult to estimate the intrinsical activity of the catalysts and to establish the kinetic of a catalytic reaction independent of the mass and heat transfer phenomena. Nevertheless, there reactors are still being used due to the existing experience in estimating catalyst performances in the standard processes within the crude oil processing industry.

III. Types of laboratory reactors for solid catalyst activity determination

Laboratory reactors used today may be classified as follows :

- closed reactors
- flow reactors, which in turn may be divided in:
  - impulse reactors, and
  - continous flow reactors

The closed reactors do not exchange materials with the exterior. In this type of reactor, the catalyst together with the reaction mixture, are located in a closed area, from where, from time to time, small samples of fluid are taken to determine the chemical transformation degree (conversion).

The impulse reactor consists of a tube in which the catalyst is placed and over which a gas is constantly passed, preferably inert to the chemical changes which are to be achieved. At certain intervals, small quantities (impulse) of reactants are introduced into the gas stream. The reaction products, formed during the passage of the impulse over the catalyst layer, are analysed with an analytic instrument at the reactor outlet. Such a reactor may also be by using, for this purpose, the column of a gas chromatograph filled with the catalyst being studied.

These two types of reactors, briefly described above, are especially used for preliminary studies, the closed reactors especially for non-catalized reactions or homogeneous catalysed, while the impulse reactors are used to elucidate the mechanisms of reaction or to study the effects of various inhibitors, poisons or promotors.

In laboratory practice, reactors with continous flow of feed stock are more frequently used. The methods elaborated between 1930 and 1960, which were developed in the same time with the crude oil catalytic processing methods, such as gasoline cracking, hydrefining and reforming, were based on the use of integral reactors. Today, there is a tendency to extend the use of differential reactors in research work to elaborate new catalysts, or improve the existing ones, as well as for the usual control of catalyst fabrication and operation.

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Similitude to differentia_ conditions is achieved in several ways, the main steps taken referring to :

-achievement of a fast flow over the catalyst layer (Re_p higher than 30), the pressure drop along the catalyst layer being prohibitive;

-use of the smallest possible catalyst particles to avoid internal diffusion, the limitation also being the pressure drop along the catalyst layer ;

-catalyst dilution with an inert material ;

-reactnat dilution ;

-experimenting at low conversions, the only limit being in this case the sensitivity and accuracy of the reaction product method of analysis.

The laboratory reactors differs by constructive and functional characteristics and one may distinguish the following types:

-fixed bed reactors

-fixed bed reactors with reactant recirculation;

-reactors with fluidized catalyst ;

-rotating catalyst bed reactor.

1. Fixed bed reactors.

This type of reactor is the most simple to obtain being composed of a glass or metal tube, partially filled with catalyst, over which the reactant stream is continuously passed. Similitude to differential conditions is achieved by :

-operation at very low conversions(around 1%);

-dilution of catalyst with an inert material,

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especially in the case of reactions which occurs with significant thermal effects ;

- dilution of feed stocks ;
- using such a flow that the Re_p would be higher than 30.

The achievement of these conditions is seriously limited by the degree of sensitivity and accuracy of the analytical procedures, as well as the pressure drops along the catalyst layer.

In current practice such reactors are of the integral type and only in special cases experimental conditions can be achieved which could be considered as differential.

2. Fixed bed reactor with reactant recirculation

In such a reactor, the reactants are recycled over the fixed bed of catalyst by means of a pump, maintaining at the same time a continuous feed stock stream and evacuation of reaction products. A high flow rate of reactants is thus achieved over the catalyst bed, conversion being very low at a single passage (differential). A ratio between recycle rate and feed rate between 10 and 15 is sufficient to achieve experimental conditions close to the differential ones.

In spite of constructive difficulties which limit its use, this type of reactor has certain characteristics worth mentioning :

-it operates in conditions very similar to those of a differential reactor ;

-liniar velocities of the fluid stream over the catalyst bed are very similar to those of the commercial reactor ;

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- it does not require an exceptionally sensitive analytical method.

The use of this type of reactor is not recommended when secondary homogenous reactions can occur. It is true that the circuits through which recirculation is carried out are dead spaces favorable to the development of homogenous secondary reactions. Cooling of these circuits in order to minimalize secondary reactions, makes it difficult to control the temperature within the reactor, reducing the accuracy of the experimental determinations.

3. Reactor with fluidized catalyst.

This type is rarely used in the laboratory although it has certain advantages, such as :

-temperature can be easily controlled ;

-extremley small sized catalyst particles can be used which practically eliminate the resistance to mass and heat transfer within the particles.

Limitation of the gas stream rate by conditions required to obtain fluidisation, produces back-diffusion danger, which may modify the kinetic data.

4. Rotating catalyst bed reactor

Such a reactor is composed of an enclosure within which there is a catalyst basket on a shaft, on which are also mounted one or more impellers. The shaft rotates at the speed chosen by the experimenter, the catalyst basket being thus rotated in the reactant stream. By means of such an experimental system, the following is obtained :

- a uniform reactant concentration and temperature within the reactor ;

- minimum inter-phase transfer phenomena even at

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low charge stock rates, because turbulence is produced exclusively by the rotation of the catalyst bed and is thus independent of the feed rate ;

- conditions to study the influence of the physical phenomena upon the rate of reaction, variation of the speed with which the catalyst basket rotates being sufficient for this purpose.

From the data published to date, it seems that this type of reactor is more appropriate for the operating conditions prescribed for the differential reactor, its use being, therefore, indicated to study the kinetics of heterogenous catalyst reactions and to compare the performance of different catalysts. The realisation of such a reactor, especially when it is desired to operate under pressure, requires high technical skill, thus limiting the use of it.

When choosing the type of reactor, all the above considerations and reactions studied must be taken into account as well as the possibilities of practical achievement. Interpretation of the experimental data is a very delicate problem as false conclusions may be reached especially when the differential reactor conditions are not completely fulfilled or when there is no severe control of the reaction parameters.

IV. Test reactions to estimate catalyst activity for petroleum processing

Complex feed stocks of various chemical composition are submitted to catalytic processes. Catalysts are tested under conditions very similar to industrial ones in pilot units and charged with feed stocks identical to those used in the industries. ./.

The difficulties encountered and high cost of pilot experiments, as well as the need to individually characterize the catalyst functions, have lead to the development of methods for studying the catalysts by test reactions with unitary substances.

A test reaction must be so chosen as to be more representative for catalyst characterization, in other words, the technique according to which it is carried out must be the same as that used to obtain the main reactions in the industry in the presence of the respective catalyst. It is recommended that the following considerations be taken into account when chossing a rest reaction:

-choose a single reaction and avoid parallel or consecutive reactions ;

-the selected reaction should be thermodynamically as possible complete;

-the reaction must not change too much the catalyst, so that its activity is maintained constant during the reaction cycle ;

-reaction products to be analysed as quickly und accurately as possible.

In the crude oil processing industry the main catalytic reactions are cracking, isomerization, that take place by an acid mechanism, and hydrogenation and dehydrogenation reactions, catalysed especially by metals, metallic oxides or sulphides. Bi-functional catalysts must not be ommitted, with acid and metallic functions, which catalyse cracking and isomerization reactions, respectively hidrogenation-dehydrogenation reactions, that occur simultaneously.

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In order to characterize catalyst activity, representative reactions are selected, either acid catalysed, either metal catalysed. Below are given a few examples of test reactions, catalysed by active acid centres.

The non-crystalline or crystalline silica-alumina cracking catalysts are tested by cumene cracking or by conversion of a linear or branched paraffinic hydrocarbon.

The isomerization catalysts are characterized by their activity in paraffinic or alkylaromatic hydrocarbon izomerisation (for exemple n-pentan or xylene izomerization).

Acid supports used for the preparation of different catalysts are also characterized by their capacity of catalyzing double bond isomerization or of some hydrocarbon chains (ex. : isomerization of cyclohexane at methyle - cyclopentane).

All these reactions are tests to estimate the main function of the above catalysts, that is, their acid function, and finally, their specific activity.

Test reactions of aromatic hydrocarbon hydrogenation or dehydrogenation of cycloparaffines, are the criteria for estimating the metallic function of hydrocracking and reforming catalysts.

Finally, hydrogenolysis reaction of some sulphur compound (such as thiophene) or nitrogen compound (such as pyridine) are tests to estimate the desulphuration, respectively denitration activity of the catalysts used for the purification of petroleum fractions by hydrogen treating (hydrofining).

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The test reaction conc pt, which is a simplification of the real case, is of great aid in solving certain problems regarding the selection of catalysts and catalytic systems and in some simple cases (hydrogenolysis reaction of sulphur or nitrogen compounds) can even be used for scale-up problems. This concept must be carefully applied when dealing with the characterization of bifunctional catalysts as it may somdtimes lead to a harmful over simplification. Thus, in the presence of hydrocracking or reforming catalysts, made up of a support with acid function and a metal in elementary form (sometimes in oxidic or sulphur form), simultaneous reactions take place, catalysed by the acid function and metallic function of the catalysts. Reactions, such as paraffine isomerization or aromatisation, occur through a mechanism in which the presence of both functions of the catalyst is required. Estimation of the activity of such a catalyst only through the test reaction of only one of the functions is not correct. It is also necessary to effect a reaction which would be representative for the catalyst as a whole in order to obtain a correct picture of its activity. For this reason, for bifunctional catalysts, relatively complex test reactions are also used, such as conversion of normal paraffines with more than six carbon atoms. Thus, in the presence of gasoline reforming catalysts, of the Pt on alumina type and under hydrogen pressure, the heptane is transformed by hydrocracking into low molecular weight hydrocarbons, it is isomerised and dehydrocyclised to toluen. Such a test reaction, apparently selected in contradiction with the selection principles mentioned previously, is required to characterise certain catalysts of this type with complex functions.

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V. Standard methods for industrial catalyst activity determination

For the purpose of characterizing the catalyst activity in the main petroleum refining processes, standard methods have been elaborated which, in many cases, are the basis either of commercial actions, or current control of commercial plants.

The standard methods have, as a common factor, the fact that the petroleum fractions used as feed are reoresentative with respect to source, composition or catalytic process. These methods are carried out in continuous system under operating conditions similar to those applied in the industry.

Catalyst activity and selectivity is expressed in terms of technological or commercial interest such as the most interesting product yield or one of the key product representative charactoristic of the process such as a property or composition of the product. In many methods, in order to simultaneously express the catalyst selectivity, these characteristics are dependent on operating condition prescriptions or are correlated with the respective product yields.

It stands to reason that in order to obtain representative data in this manner, deep conversion must be effected, close to thermodynamical equilibrium, as is done in commercial plants. For this purpose the operating conditions of these standard methods, place the reactors in the integral group. The conditions for the competent estimation of data obtained are: strict observance of the experimental parameters, charge stock and

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key product processing conditions as well as ample knowledge regarding the behaviour of catalysts in different sized plants and industrial reactors. As in the case of catalysts and petroleum refining processes there is such an experience, the standard methods are useful and are used on a large scale. To this is also added the possibility adopted by some of these methods of effecting determinations in comparison with a known catalyst taken as a standard.

A brief summary is given below regarding the principle, operating methods and expression of catalyst activity and selectivity by these methods.

A relatively high number of methods have been prepared by various companies in different countries to characterise cracking catalysts, using varied operating conditions:various speed rates, charge stock/catalyst ratio, temperature and cycle time, In all cases heavy distillate cuts are cracked, especially atmospheric distillation gas oil obtained from a well-known crude (East-Texas or Mid-Continent, etc). Fixed bed as well as fluidizedbed catalysts are used, the tendency being - in conformity with the nature of the industrial process - to generalize the fluidizedbed catalyst procedure.

Activity is expressed by the so called " activity index" which differs from one method to another. In most cases, the activity index represents the proportion of hydrocarbons, with boiling temperature below 200°C, in the liquid product obtained by cracking under procedure conditions, plus distillation losses (D + L). In other procedures, the activity index represents gasoline yield with distillation up to 200 or 210°C as compared to the feed stock processed. Many times this activity index is related to that obtained with a standard catalyst.

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It must be pointed out that for the determination of the fresh cracking catalyst activity index, steps are taken to eliminate errors resulting from the analysis of initial catalyst activity. For this purpose the catalyst is brought to a constant activity level, somewhat corresponding to the equilibrium catalyst activity in industrial plants, either by steam treatment or consecutive reaction-regenerating cycles.

No special methods have been developed regarding the characterization of catalyst activity and selectivity for gasoline reforming and aromatisation catalysts, although the literature is very rich in describing the performance of these catalysts. However, the catalyst manufacturing or oil processing companies of various countries have developed their own methods. This state of affairs is party explained by the high cost of equipment as well as of the work itself, which is prohibitive for activity determination in certain refineries which, in case of need, contact the specialized companies.

Reforming catalyst activity and selectivity are characterized by the reformed product octane number (gasoline stabilized by debutanizing or even depentanizing) obtained by processing, in conditions similar to commercial ones, a standard atmospheric distillation gasoline. Expression of reforming catalyst activity and selectivity also takes into account the stabilized reformed gasoline yield, content of aromatic hydrocarbons in the resulting product, in correlation with prescription regarding process feed-stock and operating conditions (temperature, pressure, space rate, hydrogen/feed stock ratio, etc.).

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[illegible] catalysts are tested in units under hydrogen pressure, similar to commercial ones. Hydrotined products are chemically analyzed after reacting, hydrogen sulphide, water or [illegible] ammonia resulting from hydrogenolysis reaction of S, N and O compounds in the processed oil cut.

Catalyst activity is expressed by the degree of desulphuration, denitration, deoxygenation, which represent the ratio between the respective contents of sulphur, nitrogen, oxygen of the feed stock and product, expressed in percentages. In order to ensure repeatibility of determinations, it is absolutely necessary to work with the same feed stock as the large variety of heterocompounds from the oil cuts and their reactivity is well known. Many times it is preferable, in this case as well, to compare the performance with that of a standard catalyst. It must also be pointed out that in the estimation of hydrofining catalysts activity other commercial characteristics of the product are used, such as colour, colour stability or product odour.

VI. Conclusions

In conclusion to the above, it may be shown that the actual state of knowledge regarding characterisation of catalyst activity indicates that it would be desireable to test the catalysts in differential reactors in view of selection based on intrinsical activity. On the other hand, also with the use of differential reactors, kinetic studies can be carried out from which would result the rate of the chemical reaction without the influence of mass and heat transfer phenomena. There are premises for the application of test reaction studies to the design of

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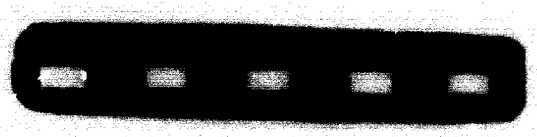
commercial units where relatively simple catalytic reactions occur, which, unfortunately, is not the case in crude oil processing. To date, in order to obtain design data for oil processing catalytic plants, studies must be carried out in various steps, including pilot units, as the simplifying data obtained by test reactions are not sufficient to design a catalytic reactor. An exception is the hydrofining process, relatively the simplest, where the data obtained by test reactions were actually used to design commercial reactors.

On the other hand, despite the empiric or conventional character of the so-called standard methodes for determining industrial catalyst activity, these procedures are still being used on a large scale as technological data are furnished, easily accessible to those who use industrial catalysts.

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