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NEW TECHNIQUES IN ECONOMIC

EVALUATIONS OF CATALYST EFFICIENCY

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CONTENTS

		Page
1.	Introduction	3
2	New techniques in economic evaluation of catalyst efficiency	4
2.1	Field ionization mass spectrometry	4
2.2	Infrared spectroscopy	5
2.3	Electron spectroscopy	6
2.4	Gas chromatrography	8
2.5	A theoretical approach	10
	List of references	15

1- INTRODUCTION

The problem of examining the efficiency of catalysts is encountered in several cases.

a) **in usage of catalysts for technical processes or laboratory scale experiments**

Usually, there is no need for new techniques in evaluating a catalyst during its usage as the yield pattern of a catalyzed reaction and its change due to the operating conditions or aging of the catalyst show directly its efficiency.

b) **in planning a specific catalytic process:**

Relying upon the experience of the vendor or other users the planner will select the most convenient among different catalysts with **guaranteed efficiency** without testing the catalyst itself.

c) Before and during and after production on a commercial scale catalysts are tested carefully to be able to give the requested guarantee. These final tests are expensive as the equipment used must allow the catalyst to be tested under normal process conditions regarding temperature, pressure, heat exchange, space velocity, catalyst to reactants ratio, and quality of the catalyst and feed stock.

d) **in search and development of suitable catalysts:**

Most techniques for testing catalysts efficiency had been developed for this area of activities. There is a wide range from micro catalytic scale up to pilot plant tests.

All these techniques attempt to predict catalyst activities desired for specific reactions.

The properties normally used for such predictions are:

surface area
pore volume
pore size
pore size distribution, and
reactivity

All techniques allowing the determination of one or more of these

properties as well as those techniques which deal with the determination of the interactions of reactants with a catalyst based on the mentioned properties may serve as a tool for the evaluation of catalysts efficiency.

2- **New techniques in economic evaluations of catalyst efficiency**

Considering heterogeneous catalysis, only.

2.1- **Field Ionization Mass Spectometry:**

This technique offers the possibility of ionizing the molecules of the gas phase, at a pressure of about 10^{-4} torr, which are in interaction with a catalyst by means of high electric fields and to analyse them by mass spectrometry.

Although not new as a technique, its application to catalysts evaluation has been described by W. A. Schmidt in 1968 [1] [2] with regard to the NH_3 synthesis and its possible intermediate products.

Table 1 shows various ion types and their relative intensity obtained by field ion mass spectrometry of NH_3 on iron.

Ion type	Relative Intensity	Ion type	Relative Intensity
N_2^+	1.0	NH_3^+	2.3×10^4
N_2H^+	5.0×10^3	NH_4^+	1.0×10^6
$N_2H_2^+$	3.5×10^1	$NH_4^+ NH_3$	2.85×10^3
$N_2H_3^+$	1.0×10^2	N_4^+	1.2
$N_2H_4^+$	1.0×10^1	N_4H^+	1.0
$N_2H_5^+$	3.3×10^1	$FeN_4H_n^+$	1.0-10.0
$FeN_2H_n^+$		$0 \leq n \leq 12$	
$0 \leq n \leq 6$			
N_3^+	3.5		
N_3H^+	2.5		
$N_3H_2^+$	6.5		
$N_3H_4^+$	1.5		
$N_3H_5^+$	1.0		
$FeN_3H_n^+$	1.0-10.0		
$0 \leq n \leq 9$			

Table 1: Ion types in the field ion mass spectrum of NH_3 on an iron tip (Field strength 10^7 V/cm).

Important is the high intensity of the NH_3^+ and NH_4^+ ions and the absence of NH_2^+, NH^+ and N^+ ions. Schmidt investigated the field ion mass spectrum on NH_3 on platinum, too. Under similar conditions only ion structures of PtN_x^+ ($0 \leq x \leq 6$), PtN^+ were found. No hydrogen was present in these ions.

The high efficiency of iron in this experiment is evident!

2.2- Infrared Spectroscopy

This well known technique was also used by Nakata and Matsushita (3) who found after adsorption of N_2-H_2 mixtures and NH_3 on a Fe-SiO_2 catalyst at higher temperatures only NH and NH_2 surface

complexes. According to Jiru (4) better results will be obtained by replacing the SiO2 carrier by an MgO carrier, as now the strong bands of SiO_2 between 1900 and 1400 cm^{-1} are avoided. With the MgO carrier the infrared spectra of surface complexes may be measured in the range 4000 cm^{-1} to 300 cm^{-1}.

2.3- Electron Spectroscopy

This promising technique was known for 25 years as Siegbahn and co-workers analysed photo ejected electrons. (5), (6), (7) with a double focusing spectrometer. But not sooner than 1962 its general utilization began. Turner (8) reported instrumentation and studies using high resolution electron spectroscopy to determine the vibrational states of molecular ions.

But electron spectroscopy is mainly a surface technique as the average penetration of a photoelectron is about 50 Å (9).

The basic processes common to all electron spectroscopy techniques are shown in Figure 1.

Ionizing radiation causes the ejection of sample electrons. The electrons go into an electron monochromator and the energy of the photoejected electron is determined. After energy resolution by the monochromator, a signal proportional to electron intensity is read out on the detector.
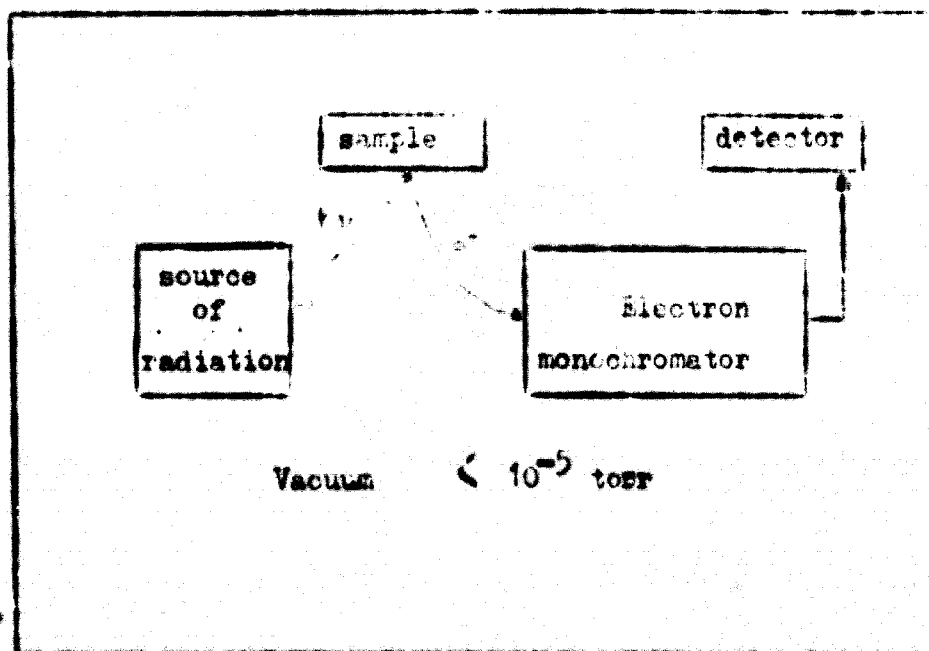
Figure 1. Schema of Electron Spectroscopy

The kind of information obtained depends upon the energy of the ionizing radiation and resolution of the monochromator. With high-energy radiation such as X-rays or γ-rays, core electrons may be ejected and their binding energies determined. With low-energy radiation, such as ultraviolet radiation, valence shell electrons will be ejected and their ionization potential determined.

This qualitative flexibility and the possibility of quantitative measurement make this technique attractive in chemical and structural analysis.

Especially, electron spectroscopy is suitable for surface studies even though a surface is covered by more than one layer of material. Also submonolayers on surfaces may be studied. Above the described advantages this technique allows the simultaneous study of the surface and the layer covering it. This is particularly interesting for catalyst studies, as the nature of changes occurring at active centres on the catalysts, as well as changes in the material being absorbed on the catalyst, may be determined simultaneously.

These advantages together with the possibilities of qualitative and quantitative analysis the electron spectroscopy will become the future technique in evaluating catalysts efficiency.

2.4- Gas chromatography

Gas-solid chromatography may be used in two different ways for the evaluation of catalysts efficiency.

a) the catalytic pulse methods, developed 1955 by Emmett (10), (11) which are distinguished between each other by the way of introducing the reactants to the reactor and the gas-flow system.

These techniques – the Static Pulse Method,

the Flow Pulse Method,

the continuous Flow Method, and

the Circulational Flow Method

have in common

a reactor with the catalyst to be examined,

an analytical column and

a supplementary equipment.

Reactor and supplementary equipment is mounted to a gaschromatograph which serves as an analytical tool for the determination of reaction products.

In principle, an inert gas is passed through a short catalytic bed and certain small pulses of reacting substances are metered into it under selected reaction conditions. The column and a detector are used for the qualitative and quantitative analysis of the reaction products and unchanged starting reactants, (10), (11), thus enabling the evaluation of catalysts efficiency.

A simple example, Figure 2, may illustrate the method and its evaluation (12):
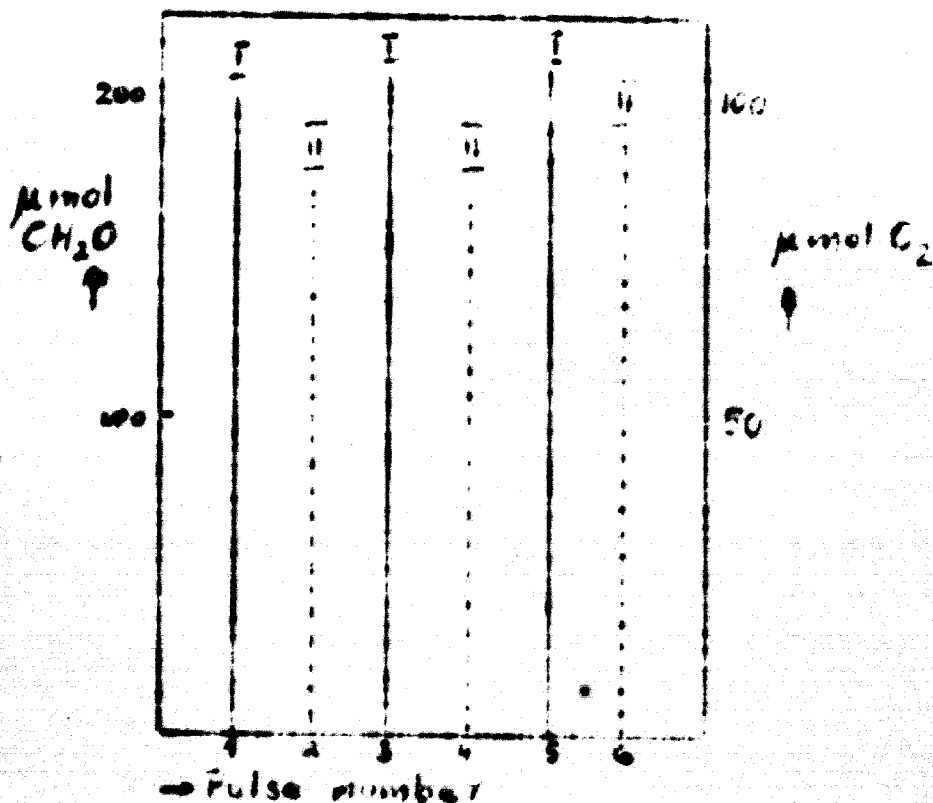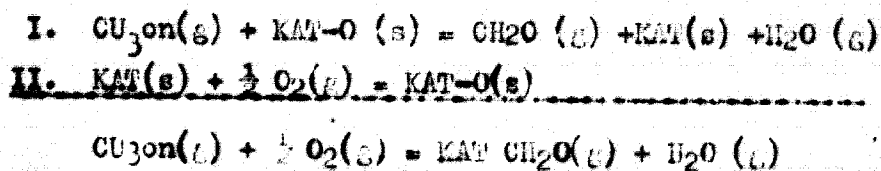
Figure 2. Pulse method, Catalyst Fe-Mo-O

Catalyst oxidation of methanol at $270^{\circ}C$,

I: CH_2O formed after a pulse of methanol,

II: O_2 consumed after a pulse of oxygen.

This example shows a two-step oxidation - reduction mechanism

$$\text{I.} \quad CU_3on(g) + KAT\text{-}O\ (s) = CH2O\ (g) + KAT(s) + H_2O\ (g)$$
$$\underline{\text{II.} \quad KAT(s) + \tfrac{1}{2} O_2(g) = KAT\text{-}O(s)}$$
$$CU_3on(g) + \tfrac{1}{2} O_2(g) = KAT\ CH_2O(g) + H_2O\ (g)$$

In the catalytic oxidation of methanol on an Fe-Mo-O catalyst:
In the first step (I) with a pulse of methanol is reduced in the **absence of gaseous oxygen**; the methanol itself is oxidized to **formaldehyde** by the lattice oxygen of the catalyst (KAT-O). In the following step (II), with a pulse of oxygen in the absence **of methanol** the reduced part of the catalyst is reoxidized showing the corresponding oxygen consumption.

Such experiments offer the possibility of evaluating the efficiency **of catalysts.**

b) The Microactivity Method

In this technique the catalyst itself is filled in a chromatographic column, and its chromatographic properties in the presence of the reactants and products are evaluated under experimental conditions lying near the catalytic process in question.

This technique has become almost an industrial standard but may only be applied for routine evaluations.

But, as we have found (13) that the activity of carbonmonoxide converting catalysts is proportional to the retention volumes of the reactants we have modified the micro activity test for the determination of the retention volume of a reactant gas (H_2, CO_2, H_2O) at temperatures ranging from 220°C to 460°C on a Fe_2O_3, Cr_2O_3, Na_2O catalyst.

Detector was a thermoconductivity cell where the retention time of a sample gas was determined by comparing the thermoconductivity of the carrier-gas without and with a sample gas, the latter having passed the catalyst column.

The specific retention volume versus temperature curve shows a distinguished maximum at about 380°C where we found the activity maximum also.

Analogous results had been obtained also with a methane converting Ni-catalyst which was investigated in the temperature range of 200°C to 800°C. A maximum of the retention volumes was found at about 740°C where the highest activity for the methane conversion was encountered.

As this test can be made easily within 10' with about 40g catalyst (after temperature constancy) it offers a new possibility of an indirect evaluation of catalysts. The specific retention volume $RV = \frac{v \times t}{G}$ (v = gas rate in ml/sec, t = retention time, G = weight of catalyst) of each reactant of a reaction is a maximum at the temperature of the activity maximum.

2.5- A theoretical approach

Because the traditional methods used to estimate the efficiency of catalysts are very expensive and time consuming, a great effort was

made to develop new and more rapid and unexpensive techniques.
But even the micro-activity tests must be carried out at many
different conditions and the result may not be extrapolated to
a process of economic scale.

If we realize that 20,000 catalyst formulations were tried by
German researchers(17) in developing a suitable catalyst for the
synthesis of ammonia, and that all of these formulations must
have been tested we immediately understand the difficulties a
researcher is facing when he has to develop a catalyst for a
specific reaction.

For that reason a new approach is desireable. A number of
researchers (15), (16), (17) try to use the available description
of CATALYTIC PHENOMENA for a special
screening analysis, which quite often offers the possibility
to derive "working models" These working models are used to
develop a new catalyst for a specific catalytic reaction which
is called "target reaction".

The guide-lines for that approach are

    a) Rationalization, through criticism of all available
       information, from any "collective" area of interest.

    b) Choice and Development of suitable working models, which
       simplifies the problem but contains the "essential terms".

    c) Parallel studies on reactions to be investigated (target
       reactions) and reactions selected as model reactions.

    d) Establishing correlations

between target and model reactions, and between solid properties
and chemical reactivity, with emphasis on their possible "predictive"
value.

As an example, how to find correlations, the choice of oxidation
model reactions is described. At first the available activity
sequence of various oxide-catalysts is taken. F.c. Stone (18)
established the pattern of nitrous oxide decomposition, table 2.
Apparently, the activities of the various catalysts may be devided

into 3 groups:

The p-type oxides are clearly the best catalysts,
the n-type oxides are the least effective ones, and
the MgO and CaO show an intermediate behaviour.

N_2O Decomposition (18)	CO Oxidation (19)	O_2 Isotopic exchange (20)	O Atom recombination (21)
Cu_2O	CoO	Co_3O_4	CuO
CoO	Cu_2O	$Mn\ O_2$	MgO
Mn_2O_3	NiO	$Ni\ O$	Fe_2O_3
$Ni\ O$	MnO_2	$Cu\ O$	$Co_3\ O_4$
CuO	CuO	Fe_2O_3	Mn_2O_3
MgO	Fe_2O_3	ZnO	$Cd\ O$
CaO	$Zn\ O$	Cr_2O_3	$Ni\ O$
Al_2O_3	$Ti\ O_2$	$V_2\ O_5$	$Zn\ O$
$Zn\ O$	Cr_2O_3	$Ti\ O_2$	$Ti\ O_2$
$Cd\ O$	V_2O_5		$Cr_2\ O_3$
$Ti\ O_2$	Al_2O_3		
Cr_2O_3			
Fe_2O_3			

Table 2: Metal oxide catalysts in the order of decreasing
activity. (reactions without hydrogen)

The other reactions chosen, namely the Carbon-monoxide oxidation,
oxygen isotopic exchange, and recombination of oxygen show a
similar trend (14). As a first result we recognize that the
most active catalysts are those having cations with unpaired
d-electrons. The anomalous behaviour of chromium oxide is an
exception which cannot be explained with the "rule of unpaired
d-electrons". A second result of that set of reactions is the
fact that there does not occur hydrogen.

To arrive at a correct working model we have to investigate hydrogen containing reactions with the same catalysts (Table 3), too.

$C_?H_4$ Oxidation (22)	CH_4 Oxidation (23)	Hydrocarbons oxidation (24)	NH_3 oxidation (25)	H_2 oxidation (26)
Co_3O_4		Co_3O_4	Co_3O_4	Co_3O_4
Cr_2O_3	Cr_2O_3	Cr_2O_3	Cr_2O_3	
Ag_2O			$Cu\,O$	$Cu\,O$
Mn_2O_3	Mn_2O_3	Mn_2O_3	Mn_2O_3	$Mn\,O_2$
$Cu\,O$	$Cu\,O$	$Ni\,O$	$Ni\,O$	$Ni\,O$
$Ni\,O$	Co_3O_4	Fe_2O_3	Fe_2O_3	Fe_2O_3
V_2O_5		$Ti\,O_2$	V_2O_5	
$Cd\,O$		Al_2O_3	$Zn\,O$	$Zn\,O$
Fe_2O_3	Fe_2O_3	$Cu\,O$	$Ti\,O_2$	Cr_2O_3
$Ti\,O_2$	$Ni\,O$	$Mg\,O$	Al_2O_3	V_2O_5
$Zn\,O$	Ag_2O	V_2O_5		$Ti\,O_2$

Table 3: Metal oxide catalysts in the order of decreasing activity (reactions with hydrogen containing compounds).

As a result from this set of reactions we arrive at the same activity pattern as with the set of table 2. Note worthy, even the chromium oxide obeys now the "unpaired d-electrons rule".

Of course, we are aware that catalysis by oxides is a very complex phenomenon and cannot be explained in terms of a single criterion, but this observed activity pattern indicates to some extent, rules for selection of oxidation catalysts.

If we had literature available to derive also correlations regarding selectivity, surface properties and reaction conditions we could achieve a system of perfect screening of catalysts in order to save costs and time for the development or search of a
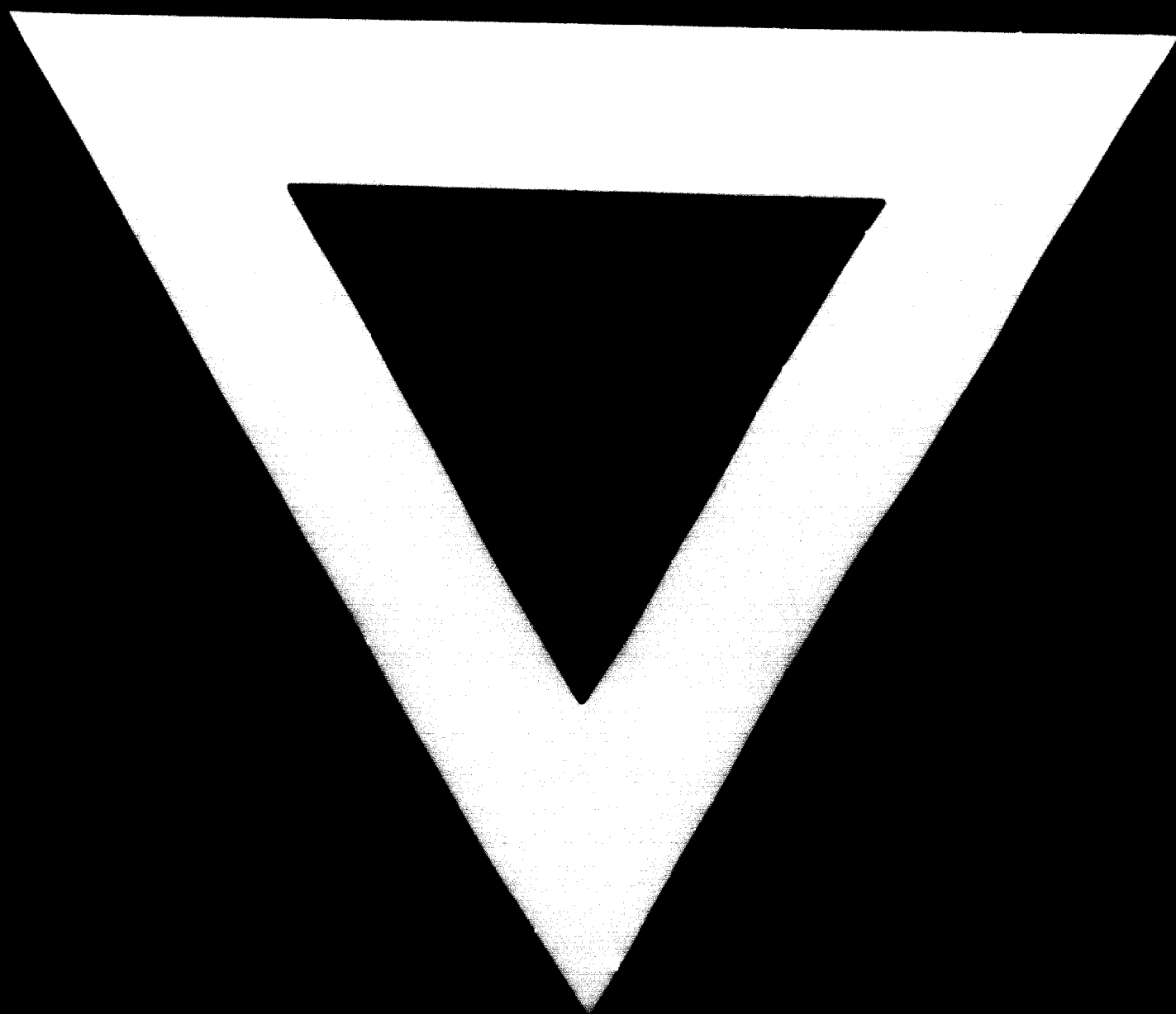
catalyst as its evaluation may be predicted for a specific reaction.

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