

A Mechanism for the Deactivation of Trace Metal Contaminants on Cracking Catalysts

R. G. MEISENHEIMER

From the Shell Development Company, Emeryville, California

Received February 10, 1962

A method is described for evaluating the extent of deactivation of heavy metal contaminants on cracking catalysts. It consists of measuring the availability of these metals for reduction by hydrogen and subsequent oxidation by oxygen. This availability very probably has a parallel in the catalytic effectiveness of these metals.

The method is then used to study the mechanisms of the trace metal deactivation. It is found that this deactivation is a selective process. Nickel is deactivated much more rapidly than iron, while vanadium is intermediate. Nickel, and probably the other contaminants as well, is deactivated only when in the oxidized form. This deactivation of the contaminants is primarily due to the formation of metal silicates or aluminosilicates and only secondarily to burial in the silica-alumina matrix during thermal collapse.

INTRODUCTION

Commercial cracking catalysts, during their life in a catalytic cracking unit, become contaminated with small amounts of various metals. These metals have an undesirable effect on the product distribution (increased coke and gas yields) (1-5). Various authors (1-5) have shown that the coke factor in a catalytic cracking unit can be related to the amount of trace metal contamination on the catalyst. It has also been shown (5) that metals content alone is not sufficient to define a coke factor for a catalyst. The various metals behave quite differently in the intensity of their deleterious effect and, as a further complicating factor, the metal contaminants lose a great deal of their effectiveness by aging in a commercial catalytic cracking unit. As an example of this behavior Small and co-workers (6) have presented a comparison of the coke production from plant equilibrium catalysts and from catalysts thermally deactivated in the laboratory to comparable activity levels and impregnated with metal compounds. They noted that the freshly de-

posited metals were much more effective for coke production than those laid down in a commercial reactor. Thus the effect of any given combination of metal contaminants will depend upon the history of the cracking catalyst sample and upon the deactivation mechanism of the metals present. This paper is concerned with the development of a method for assessing the extent of metals deactivation and the application of this method to a study of the mechanism of the trace metal deactivation.

EXPERIMENTAL

Catalyst Preparation

The artificially contaminated catalysts used in this study were all prepared in the same manner. A soluble metal salt was dissolved in 150 ml of distilled water. A 50 g sample of a fresh cracking catalyst was slurried with this solution, stirred for 1 hr, filtered, dried 16 hr at 120°C, and calcined 1 hr at 500°C. The metal salts used were $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$; NH_4VO_3 ; $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$; $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. Changes in metal content were obtained by chang-

ing the concentration of the impregnating solution. All of these solutions were less than 1% by wt metal salt. The fresh cracking catalysts were American Cyanamid commercial microspheroidal MSA catalysts. MSA-1 and MSA-2 are similar silica-alumina cracking catalysts with a typical metals analysis given in Table 2. MSA-2 contains more fines than MSA-1. MSA-3 is a high-alumina catalyst, having 21–24% Al_2O_3 , in contrast to the 12–13% Al_2O_3 present in the MSA-1 and MSA-2 catalysts. The trace constituents are not significantly different.

Reduction-Oxidation Procedure

The procedure was chosen to be as severe as possible but not so severe as to contribute appreciably to the deactivation of the metals. All samples, such as plant equilibrium catalysts, that had been subjected to cracking tests were swept with 1 atm of O_2 for a few (3–6) hours at 500°C to remove coke deposits. Every sample was swept with hydrogen at 1 atm for 4 hr at 500°C and evacuated 16 hr at 500°C . The gases used were obtained from standard cylinder supplies. The hydrogen was purified by passing through a long bed of hot copper wires to remove oxygen and then through a glass bead filled trap at liquid nitrogen temperature to remove condensables. The oxygen gas was passed through a similar glass bead filled trap held at liquid oxygen temperature. Oxygen sorption measurements were then made at 500°C to a final pressure of about 3 mm. A typical sorption isotherm is shown in

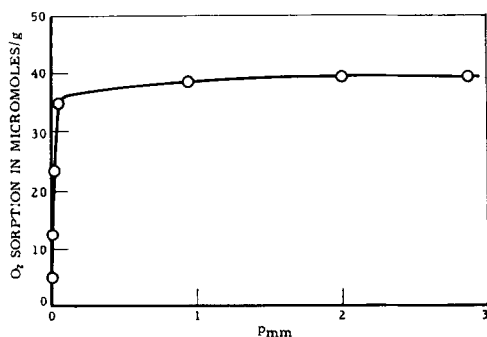


FIG. 1. Typical O_2 sorption isotherm at 500°C .

Fig. 1 and the data are presented in Table 1. Each isotherm took about one day to measure.

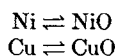
TABLE 1
A TYPICAL O_2 SORPTION ISOTHERM— O_2 ON
HEAVILY CONTAMINATED (LABORATORY)
MSA-1 CATALYST

Equilibrium pressure (mm of Hg, P mm)	O_2 sorption ($\mu\text{moles/g cat}$)
0.001	5.30
0.006	10.64
0.022	23.68
0.060	34.69
0.89	38.97
2.00	39.33
2.85	39.41

It was found for the artificially contaminated catalysts that a pressure of 3 mm of oxygen was sufficient to complete the oxidation. Several measurements were also made to demonstrate this point for the commercial catalysts. In every case, the oxygen sorption was found to be negligible after an equilibrium pressure of 1 mm had been attained. For one example, catalyst 54 contained enough metals to require 32 μmoles of O_2 for oxidation. At a 3 mm sorption measurement, it took up 14 μmoles of O_2 . At a 36 cm sorption measurement, it took up 13 μmoles of O_2 . This is good agreement in view of the decreased accuracy of the higher pressure measurement in this sorption range.

Reduction-Oxidation Stoichiometry

Before these oxygen sorption measurements can be interpreted in terms of metals "availability" it is necessary to know the upper and lower oxidation states involved. These were studied for each individual metal by measuring the oxygen sorption on freshly deposited metals of artificially contaminated catalysts. The measurements for nickel and copper showed a correspondence between oxygen consumed and oxygen required for the two reactions:



For example, an artificially contaminated cracking catalyst, MSA-1 + 0.13% Cu, was swept for 1 hr at 500°C with hydrogen to reduce the copper to the metallic state. An oxygen sorption isotherm was then measured at 500°C and 10.0 μ moles of O₂ per gram of catalyst were sorbed. This is in good agreement with a theoretical value of 10.23 μ moles per gram of catalyst expected for complete oxidation of 0.13% Cu to CuO.

In the case of vanadium, under equilibrium conditions, the bulk material would be expected to be V₂O₅ in the presence of oxygen at 500°C and V₂O₃ in the presence of hydrogen at 500°C (?). Measurements on the fresh artificially contaminated catalysts demonstrated that the reaction is most probably V₂O₃ \rightleftharpoons V₂O₅. However, these measurements also showed that the standard reduction of 4 hr at 500°C resulted in only about 70% reduction. Only by increasing the time or temperature of the treatment with hydrogen could 100% reduction be achieved. For commercial catalysts, where vanadium is usually a minor constituent, an error of this magnitude would not invalidate the results.

For iron, the work on freshly deposited metals showed an excellent correspondence between oxygen sorbed and oxygen required for the reaction Fe \rightleftharpoons FeO. In addition, an electron spin resonance study of these iron contaminated catalysts in the oxidized state (following an oxygen sorption measurement) pointed to the presence

of ferrous iron with a little Fe₃O₄ and no Fe₂O₃.

RESULTS AND DISCUSSION

A. The Method for Assessing the Degree of Metal Contaminants

After it had been demonstrated that the oxygen sorption method measured the bulk availability of the metal contaminants, it was necessary to determine whether this availability was meaningful in terms of the catalytic properties of the metals.

A commercial equilibrium catalyst was examined for its oxygen sorption properties. Its contamination level was then markedly increased by cracking a very heavily contaminated stock and the oxygen sorption measurement was repeated. The catalyst was then aged for several cracking and regeneration cycles, using a low metal content feed stock. The oxygen sorption was again measured on this sample. The trace metal analyses, oxygen sorption data, and the coke factor, C_F , (carbon % wt, basis feed) are given in the accompanying table for these samples (54, 54A, and 54B). It can be seen from Table 2 that less than one-half of the metals on the equilibrium catalyst are available for oxidation. It can also be seen that all of the freshly deposited metals on 54A are available and that continued cracking deactivates these freshly deposited metals (sample 54B). It is particularly interesting to note that changes in the total

TABLE 2
OXYGEN SORPTION AND COKE FACTOR ON COMMERCIAL CATALYSTS

Sample	Trace metals (%)					μ Moles O ₂ required for total oxidation ^a	μ Moles O ₂ sorption	Metals unavailable	C_F
	Fe	Ni	Cu	V	Cr				
53, Fresh MSA-2	.040	.0008	.002	< .001	.002	3.8	2.2	1.6	2
215, Equilibrium	.380	.032	.016	.047	.0049	43	17	26	7.4
197, Equilibrium	.270	.063	.0036	.054	.0039	35	18	17	6.5
54, Equilibrium	.300	.034	.0026	.025	.0041	32	14	18	5
54A, 54 + Contamination	.400	.096	.0115	.092	.0055	54	34	18.6	12.5
54B, 54A + Aging ^b	—	—	—	—	—	54	32	22	10.5

^a Assuming all metal available for reduction and subsequent oxidation.

^b No significant change in metals content was made by the aging process.

amount of available metals are paralleled by changes in the coke factor.

If the concept that the oxygen sorption measures the available, catalytically active metals is valid, a better correlation

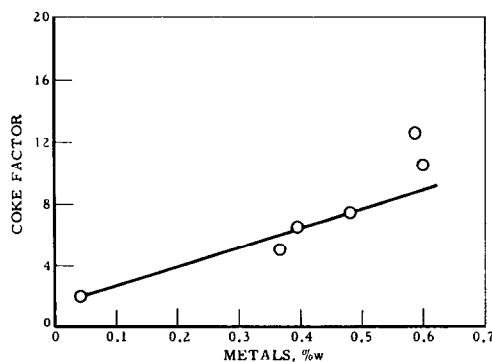


FIG. 2. Correlation of coke factor with total metals.

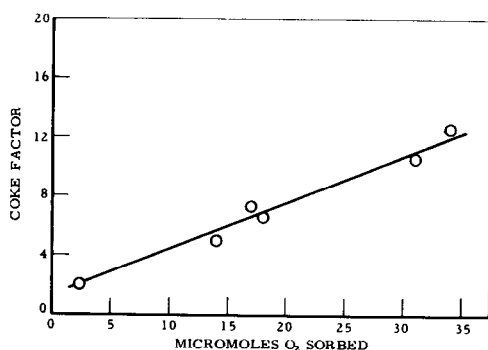


FIG. 3. Correlation of coke factor with available metals.

might be expected between cracking properties and available metals than between cracking properties and total metals. Such correlations are shown in Figs. 2 and 3 for the data of Table 2. It is apparent from these figures that the available metal correlates at least as well with C_F as does total metal. In addition, the measurements on samples 54, 54A, and 54B show that changes in available metals can explain differences in cracking behavior that are not explainable on the basis of total metals.

B. The Mechanism for the Deactivation of Metal Contaminants on Cracking Catalysts

When the thermal deactivation of trace metals deposited upon a cracking catalyst is considered, two mechanisms seem most probable. One is the thermal burying of the metals in the silica-alumina matrix during the sintering process. The other is the formation of metal silicates or aluminosilicates with the substrate. The work described here was undertaken to determine the relative importance of these two mechanisms for the formation of "inactive" metals.

Effect of sintering upon the deactivation of trace metal contaminants. If sintering is the most important deactivation mechanism, we would expect a correlation between the decrease in surface area and the decrease in available metal. In Table

TABLE 3
OXYGEN SORPTION DATA ON MSA-1 + 0.22% Fe^a

Treatment	Surface area	Fraction remaining	O ₂ sorption, μ moles/g	Fraction remaining
3½ hr 576°C Air	580	0.95 ^b	17.6	.90
3 hr 825°C Air	288	.47	12.1	.62
16 hr 825°C Air	264	.43	11.5	.59
42 hr 950°C Air	33	.05	12.5	.64
3½ hr 576°C Air	290	.48	17.0	.87
+44 hr 576°C Steam				
21 hr 825°C Vacuum	480	.79	12.4	.64
21 hr 825°C Vacuum	223	.37	11.2	.58
+20 hr 576°C Steam				

^a Thirty-nine μ moles iron per gram of catalyst, requiring 19.5 μ moles O₂ per gram of catalyst to form FeO.

^b Original surface area, 610 m²/g, after 4 hr, 500°C, air.

3, the experimental data on Sample 1, MSA-1 + 0.22% Fe are presented.

It can be seen from this table that no parallel exists between available metals decrease and surface area decrease. Severe calcination at 950°C decreased the surface area to 5% of its original value while decreasing the available metal to 60% of the original value. Also, steam treating the catalyst to make large decreases in the surface area had virtually no effect on the available metals.

This conclusion was confirmed by measurements on two other samples; the results are presented in Table 4.

amine the mechanisms responsible for surface area decline. These mechanisms have been discussed in papers by Schlaffer, Morgan and Wilson (8) and by Adams and Voge (9). These authors show that the mechanism for surface area loss in low temperature steaming is a growth of large particles at the expense of small ones. Surface tension forces are important in regulating this growth since the final particles are still spherical. The mode of transport has been shown to be, most probably, via either the vapor phase or surface diffusion. Since this deactivation process is concerned with the breaking and reforming of the

TABLE 4
OXYGEN SORPTION DATA

Treatment	Surface area (m ² /g)	Fraction remaining	O ₂ sorption (μmoles/g)	Fraction remaining
<i>MSA-2 + 0.35% Fe^a</i>				
4 hr 500°C Air	509	1.00	33	1.00
16 hr 700°C Air	439	0.86	29	0.88
24 hr 900°C Air	181	0.36	20	0.61
<i>MSA-2 + 0.34% Ni^b</i>				
4 hr 500°C Air	546	1.00	26	1.00
23 hr 500°C Air	523	0.96	18	0.69
24 hr 900°C Air	169	0.31	2	0.08

^a Sixty-three μmoles of iron per gram of catalyst, requiring 31½ μmoles of O₂ per gram of catalyst to form FeO.

^b Fifty-eight μmoles of nickel per gram of catalyst, requiring 29 μmoles of O₂ per gram of catalyst to form NiO.

Here again it can be seen that the decrease in surface area is not accompanied by a corresponding decrease in available metals. It should also be noted that nickel is deactivated much more rapidly than iron. This specificity provides very strong evidence against the thermal burying mechanism since such a mechanism would be expected to be dependent only upon the time and temperature of treatment and not upon the specific metal present.

The above measurements thus show that neither high temperature thermal deactivation nor low temperature steam deactivation results in metal deactivation comparable with the loss in surface area. To digress for a moment in order to discuss what this may mean in terms of the physical structure of the catalyst we first ex-

bonds binding together the silica-alumina substrate, the metals present can apparently assume the role of a bystander and their disposition and availability come through the process unaffected.

High temperature deactivation, on the other hand, appears to be due to local volume fusion of adjacent particles, this process spreading throughout the mass. Volume fusion of two particles would decrease the total surface area but would not require the burying of metal particles on the original surfaces.

A process that would require a decrease in metal availability is that which leads to the "glazed" particles found in some commercial reactors. Here, a particle sinters on the outside, forming a nonporous shell around the unsintered material with-

in, making the surface area, pore volume, and trace metals of this trapped material unavailable.

An interesting point from the above data is the apparent lower limit of about 12 μ moles of sorbed oxygen per gram of catalyst observed for the iron impregnated sample. This lower limit for the available metal can be explained if we visualize two simultaneous processes occurring. The metal is deposited as many small aggregates about the silica-alumina surface. When the temperature of the catalyst is raised, the metal absorbs energy and the atoms associated with the smaller aggregates then do one of two things. They migrate over the surface until they either form a chemical combination with the substrate or attach themselves to a larger crystallite of metal or metal oxide. Silicate formation would then stop when, under given temperature conditions, all of the metal atoms not bonded to the substrate are attached to metal or metal oxide crystallites so large that they no longer can acquire sufficient thermal energy to be removed from the crystallite. Such a crystallite growth process would in itself result in a decreased catalytic effectiveness for the metals, due to a decreased surface area.

Specificity of the deactivation of trace metal contaminants. It was pointed out above that a specificity exists for the extent of deactivation wrought by a common heat treatment for iron and nickel. A series of measurements was made to determine the relative ease of thermal deactivation (as measured by O_2 sorption) of the three metal contaminants of primary importance, Fe, V, and Ni. These measurements were made on artificially prepared samples with a single metal present in each case. The results are presented in Table 5.

A considerable variation in the degree of deactivation of the three metals under identical thermal treatment can be noted from this table. Iron is the most difficult to deactivate, nickel is the easiest, while vanadium is intermediate. This would indicate that selective deactivation probably occurs on a catalyst in a commercial cata-

TABLE 5
RELATIVE AVAILABILITY OF DEACTIVATED
NICKEL, VANADIUM, AND IRON

Sample	4 hr 500°C Air	23 hr 500°C Air	24 hr 700°C Air	24 hr 900°C Air
MSA-2 + 0.35% Fe	97	87	61	58
MSA-2 + 0.34% Ni	79	62	24	7
MSA-2 + 0.34% V	86	42	42	32

lytic cracking unit. It might be presumed from these data that nickel is a less important contributor to catalyst contamination than would be indicated by metal analysis alone.

Effect of chemical state of the metal upon deactivation. All of the above evidence points away from the physical burial of the contaminants as the deactivation mechanism and toward the contention that the formation of a silicate or aluminosilicate is the deactivation reaction. If this conclusion is correct the rate of deactivation should depend markedly upon the chemical state of the metal. An ionic compound such as NiO would be expected to form a silicate when heated with SiO_2 much more rapidly than would nickel metal. The measurements presented in Table 6 provide a test of this statement.

TABLE 6
MICROMOLES O_2 SORBED ON MSA-3 + 0.59% Ni
AFTER TREATMENT AT 500°C
IN VARIOUS ATMOSPHERES

Treatment atmosphere	Ni Metal	O_2 sorption ^a	NiO
H ₂	54		54
CO	52		52
H ₂ S	52		52
Vacuum	52		15
N ₂	50		32
O ₂	33		25
Air	26		16
Air + Steam	14		15

^a Fifty μ moles of O_2 are required to oxidize the nickel on a gram of this catalyst.

These measurements were made on samples of an artificially contaminated cracking catalyst. MSA-3 + 0.59% Ni was cal-

cined one hour at 500°C and divided into two equal parts. One-half was swept with hydrogen for 3 hr at 500°C to convert the contaminant to metallic nickel; the other half was left as nickel oxide. Aliquots of each sample were heated for 16 hr at 500°C in the various atmospheres listed in Table 6. The amounts of oxygen sorbed after these pretreatments (and the usual hydrogen reduction) are also given in Table 6.

One fact is immediately apparent from these data; the nickel metal must be in the form of nickel oxide for deactivation to occur at 500°C. In every instance of heating in a reducing atmosphere no loss of metal availability occurred. In every instance of heating in an oxidizing atmosphere a loss in metal availability did occur. When the samples were heated in inert atmospheres no loss of metal availability occurred if the nickel was in the metallic form; a loss did occur if the nickel was present as an oxide. These results can be cited as further evidence in favor of silicate formation as the deactivation mechanism. If thermal burial were important we would expect the above observed effects to be very different. For example, the effect of vacuum heating is strikingly different for the reduced and oxidized forms, a result at variance with a thermal sintering process.

CONCLUSIONS

It has been demonstrated that changes in the effectiveness of the metal contaminants on individual cracking catalysts can be followed by the oxygen sorption method. Using this method as a tool the following conclusions have been drawn concerning the deactivation process:

The deactivation of heavy metal contaminants on the cracking catalyst in a catalytic cracking unit is a thermal process, increasing with increasing time and temperature of exposure.

This deactivation is a selective process. Nickel is deactivated much more readily than iron, while vanadium is intermediate.

Deactivation occurs for nickel, at least at moderate temperatures, only when the element is in the oxide form. This would indicate that deactivation for the reducible metals occurs during the regeneration cycle in the unit.

The deactivation of the contaminants is probably due to the formation of metal silicates or aluminosilicates and only secondarily to burial in the silica-alumina substrate during the sintering process.

ACKNOWLEDGMENTS

We wish to thank W. B. Wilson for providing the commercial catalysts samples and the cracking data (C_F) used in this paper and for many valuable discussions of this work. We wish to thank W. G. Schlaffer for all steam treatments performed upon our samples. We also wish to express our appreciation to Miss Edna F. Dean for valuable discussions and assistance with the measurements.

REFERENCES

1. GOSSETT, E. C., *Petrol. Refiner* **39**, 177 (June, 1960).
2. ROTHROCK, J. J., BIRKHIMER, E. R., AND LEUM, L. N., "Fluid Cracking Catalyst Contamination. I. Development of a Contaminant Test," *Symposium on Techniques of Catalyst Preparation*, Am. Chem. Soc., Dallas, Texas (April 8-13, 1956).
3. SHANKLAND, R. V., *Advances in Catalysis* **6**, 378 (1954).
4. MILLS, G. A., *Ind. Eng. Chem.* **42**, 182 (1950).
5. DUFFY, B. J., AND HART, H. M., *Chem. Eng. Prog.* **48**, 344 (1952).
6. SMALL, N. J. H., KIRKALDY, P. H. S., AND NEWTON, A., *Proc. Fourth World Pet. Congress, Section III*, p. 261. Rome, 1955.
7. KOMAREWSKY, V. I., AND COLEY, J. R., *J. Am. Chem. Soc.* **70**, 4163 (1948).
8. SCHLAFFER, W. G., MORGAN, C. Z., AND WILSON, J. N., *J. Phys. Chem.* **61**, 714 (1957).
9. ADAMS, C. R., AND VOGEL, H. H., *J. Phys. Chem.* **61**, 722 (1957).