PERFORMANCE OF SUPPORTED NICKEL CATALYSTS IN CYCLIC STEAM REFORMING OF NATURAL GAS

by
J. M. Reid and D. M. Mason
Institute of Gas Technology
Chicago, Illinois

ABSTRACT

Comparatively little data are available regarding the performance of catalysts in the cyclic steam-hydrocarbon reforming process used by the utility gas industry on the Eastern Seaboard, and more extensively in Europe and Asia. In this study, several commercial types of supported nickel catalysts having either alumina or magnesia as the base material were subjected to cyclic process conditions in a laboratory reforming apparatus. Catalyst performance and catalyst life were significantly affected by the oxygen which was present during the heating portion of the cycle. Unlike the continuous steam-hydrocarbon reforming process used extensively by the chemical industry for production of hydrogen and ammonia synthesis gas, performance of the cyclic process was not found to be singularly dependent on the activity of the catalyst for the steam-hydrocarbon reaction, but rather under certain conditions to be controlled by the rates of oxidation and reduction of the nickel. In these tests, life of alumina-supported catalyst was related to the formation of an unreactive compound between nickel oxide and the support. Life of the magnesia-supported catalyst was related to solid solution formation between nickel oxide and the support. The inadequacy of present manufacturing specifications and testing procedures for nickel catalyst for cyclic reforming is illustrated by these results.

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INTRODUCTION

Catalytic steam reforming of natural gas and other low molecular weight hydrocarbons is a well established process.[6,29,32,33,40,41] It has been applied extensively in the chemical industry where large quantities of hydrogen are required, as in the case of ammonia synthesis. A few installations have also appeared in the utility gas industry for the production of low heating value fuel gases.[1,16,21]

The process is carried out in a tube furnace in which preheated steam and hydrocarbon are passed through externally heated catalyst-filled tubes. The hydrocarbon and steam react to produce hydrogen, carbon monoxide and some carbon dioxide. This reaction is highly endothermic. Reaction temperatures range from about 1200°F. to 1800°F. and pressures from atmospheric to several atmospheres. The most commonly employed catalyst is reduced nickel oxide supported by a high surface area refractory material; nickel concentrations range from several weight percent to more than 30.

Performance of these catalysts has been extensively investigated.[5,30,31] In addition to process conditions, the major factors influencing the catalyst behavior have been shown to be poisons such as sulfur compounds contained in the feed streams, and physical properties of the catalyst such as surface area, porosity and crystallite size. With proper control of process variables, the catalyst appears to have essentially unlimited life in commercial operation.

Cyclic Reforming

Prior to World War II, the utility gas industry in the United States was based almost entirely on carburetted water gas produced from coke, steam and oil in cyclic apparatus. The availability of low-cost natural gas to major population centers through long distance pipe lines constructed in the post-war era made processes based on solid fuel economically unfavorable. Where conditions warranted the continued distribution of low heating value gas, it was necessary to find some means for converting natural gas. The catalytic steam reforming process was ideally suited for this purpose. However, the process as developed by the chemical industry is carried out in continuous tube furnaces. To adapt this process to the gas industry would require the capitalization of entire new manufacturing plants to replace the existing carburetted water gas plants. A more attractive scheme for the utilities was made possible by the United Gas Improvement Company, which pioneered the development of the cyclic reforming process in the United States.[20,26,34,35,42,44] The cyclic process could be carried out by a relatively low-cost modification of the existing carburetted water gas equipment. As a result, 17 cyclic process installations are in use in the eastern part of the United States.[13,25]

The Cyclic Catalytic Reforming (CCR) process differs from the conventional continuous process, basically, only in the manner in which the heat requirements are supplied. First, the catalyst bed located in one of the refractory-lined shells from the carburetted water gas apparatus is heated to reaction temperature by the passage of hot products of combustion supplied by either oil or gas burners. This is followed by a reforming step in which steam and hydrocarbon are passed through the catalyst bed. The heat stored in the refractory shapes used for process steam preheat and in the catalyst bed during the heating step is used during the reforming step. Steam purges are normally used to separate the heating and reforming steps. The entire cycle sequence is generally completed in less than five minutes.

The catalyst employed in the cyclic reforming process is similar to continuous reforming catalyst in that it is metallic nickel supported by a refractory material. Properties of the refractory support are necessarily more stringent for the cyclic process because of the thermal shock associated with cyclic heating and cooling of the catalyst bed and because of a tendency for the bed to lift or move slightly with cyclic flow changes. The material used almost universally in commercial operation consists of fused spheres 1/2 to 1 inch in diameter, of impure alumina (90%) having medium porosity (30-40%). The catalyst is prepared by impregnating the spherical support with a nickel salt solution and then decomposing the nickel salt to nickel oxide by heating in air to about 600°C.

Performance of the catalyst has been commercially acceptable for utility operation, but the catalyst has decidedly short life compared to catalysts used in the continuous reforming process.[25] Ordinarily more than 50% of the original catalyst activity is lost after 2000 to 4000 hours of operation with one inch diameter catalyst. For 1/2-inch diameter catalyst, where relative light catalyst loading is used, somewhat longer life is obtained. Plant capacity is obviously affected by loss in catalyst activity, and replacement of at least part of the catalyst is required annually.

Efforts to improve catalyst performance in the cyclic process have recently become of considerable interest to utility companies using the CCR process.[25] In addition, extension of the CCR process to liquid hydrocarbon operation and the development of several new gas manufacturing processes which incorporate in some form the principles of cyclic catalytic steam reforming of hydrocarbons have focused attention on the performance of catalyst under cyclic conditions.[3,11,22,28,43] In a recent study at the Institute of Gas Technology, the cyclic performance of several supported nickel catalysts was investigated under closely controlled conditions in the laboratory. It was the object of this study to determine the factors unique to the cyclic process which governed catalyst performance and were responsible for relatively short catalyst life. Significant results of this study are presented here.

EXPERIMENTAL

This study was limited to commercial catalysts containing approximately 5 weight per cent nickel. Support materials were either fused alumina (α -Al_2O_3) or fused periclase (MgO). All of the catalyst pellets were in the form of nominal 1-inch diameter spheres except for one sample with high-purity alumina support which consisted of irregularly shaped, 1-inch lumps. Only the lower purity alumina base catalyst contained magnesium oxide promoter. Properties of the

unused catalysts are shown below.

Catalyst Designation	A	B	C	D
Acid Soluble Nickel, wt. %	5.14	4.48	4.99	5.16
Magnesium Oxide Promoter, wt. %	1.81	None	None	None
Support Composition, wt. %				
Al_2O_3	86.85	99+	—— 0.3 ——	
MgO	--	--	—— 95.5 ——	
SiO_2	12.90	--	—— 3.0 ——	
CaO	--	--	—— 1.0 ——	
Fe	0.25	--	—— 0.2 ——	
Pellet Shape	Sphere	Irregular	Sphere	Sphere

Catalyst nickel concentration data appearing throughout this paper refer to that nickel portion of the catalyst which was soluble in nitric acid. The nickel content was determined by boiling a ground (minus-100 mesh) sample with concentrated nitric acid until the disappearance of brown fumes, followed by filtration and gravimetric determination by a standard dimethylglyoxime method.

X-ray diffraction patterns of the catalysts were obtained by the Debye-Scherrer powder camera method.

Reforming tests were conducted in the apparatus shown in Figure 1. The reactor consisted of a 3.125-inch I.D. x 102-inch long, Type 310 stainless steel tube with a centrally located 0.675-inch O.D. thermowell of the same alloy inserted through the bottom. The reactor tube was suspended in a Smith alloy wound electric furnace with four independently controlled heating zones. The temperature in each zone was regulated by potentiometric temperature indicator-controllers in combination with chromel-alumel thermocouples. The control thermocouple was welded to the outside skin of the reactor tube at the center of each heating zone. Additional chromel-alumel thermocouples located in the internal thermowell were used to measure the catalyst temperature at three points within the bed and the feed gas stream temperature immediately before entering the bed.

Provision was made to weigh distilled water, which was fed by a chemical proportioning pump through an electrically heated steam generator to the top of the reactor tube. Natural gas was fed from high-pressure cylinders through a pressure regulator and gas meter to the top of the reactor tube, where it was mixed with the steam feed. Product gas was withdrawn from the bottom of the reactor tube through a water-cooled tube and shell condenser, where excess steam was removed. The cooled product gas stream was measured with a second gas meter before being discharged through a back-pressure regulator to the sampling system. All measured gas volumes were corrected to standard cubic feet (SCF) at 60°F., 30 inches of mercury pressure, and saturated with water vapor. A side stream of the product gas was collected for a recording calorimeter and for Orsat and mass spectrometer analyses.

For each reforming test a 0.1 cubic foot sample of catalyst was placed in the lower two heating zones of the reactor furnace and formed a 24-inch deep bed. Inert periclase spheres were used below the catalyst to properly space the bed in the reactor tube.

The apparatus as described was suitable for conducting the continuous reforming process. For cyclic operation, additional equipment was required. Provisions were made for supplying and metering both nitrogen (for purging) and air in a manner similar to the natural gas feed system. The natural gas, nitrogen and air feed lines were equipped with electrically operated solenoid valves which were opened and closed by a repeat cycle sequence timer. The steam feed system, reactor and product gas handling system were identical for cyclic

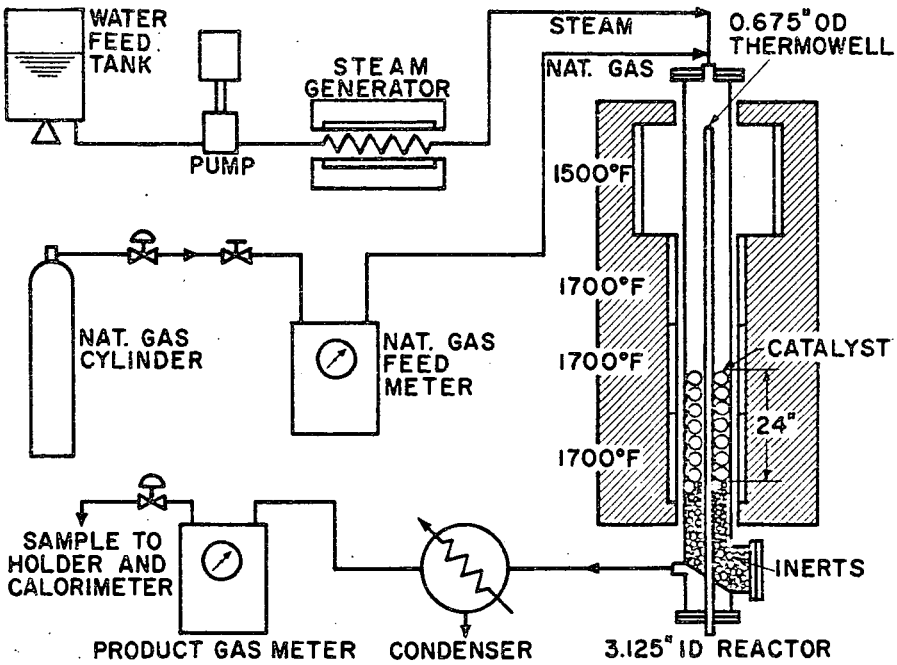

Fig. 1.-LABORATORY REFORMING UNIT

operation as for continuous reforming tests. A simple switching system made it possible to change from continuous operation to cyclic operation without interruption.

Reforming tests were long enough to insure attainment of equilibrium. The test period was normally about three to four hours after steady state was reached.

FACTORS INFLUENCING CATALYST ACTIVITY IN CYCLIC REFORMING

In the continuous reforming process the catalyst is at all times in the reduced state and at a constant temperature. The major reaction which is affected by the condition of the catalyst is that between the hydrocarbon and steam:

$$C_nH_m + nH_2O \longrightarrow nCO + (n + m/2)H_2 \qquad (1)$$

Subsequent reaction between part of the product carbon monoxide and steam has little influence on reaction (1) or on the ability of the catalyst to promote reaction (1):

$$CO + H_2O \longrightarrow CO_2 + H_2 \qquad (2)$$

The overall catalyst performance is therefore governed by the ability of the catalyst to promote the steam-hydrocarbon reaction at the temperature maintained in the catalyst bed.

Cyclic reforming is an exceedingly complex process by comparison. Neither catalyst temperature nor composition of the atmosphere remain constant. In a single cycle the catalyst is first heated, then cooled; oxidized, then reduced. The extent of these changes varies widely in actual practice. In some cases, combustion is controlled during the heating portion of the cycle so that the combustion products contacting the catalyst are essentially neutral. The quantity of catalyst which is oxidized in this instance is small. Another method of operation employs a certain amount of excess air in the combustion products to take advantage of the heat released in the catalyst bed by combustion of nickel metal.[7] Other forms of cyclic reforming require the passage of undiluted air through the catalyst during the heating cycle.[22] In all methods of operation, process heat is stored in the massive catalyst bed during the heating period for use during the make period. The catalyst, therefore, undergoes a significant change in temperature throughout the cycle.

Because of the changes in atmosphere throughout the cycle, other reactions besides reaction (1) occur in the cyclic process and are dependent upon the catalyst. Although the cyclic process is not fully understood, at least two other reactions of importance are those between metallic nickel and oxygen and between nickel oxide and a reducing agent.

$$2Ni + O_2 \longrightarrow 2NiO \qquad (3)$$

$$(2n + \tfrac{m}{2})\ NiO + CnHm \longrightarrow (2n + \tfrac{m}{2})\ Ni + nCO_2 + \tfrac{m}{2}\ H_2O \qquad (4)$$

Reaction (4) represents only the most probable stoichiometric relationship, and is not intended to indicate the actual mechanism of reduction in the process.

Other constituents of the reacting gases, such as sulfur compounds in the hydrocarbon feed, and nitric oxide in the combustion products used for heating, affect the process.

It is apparent that the overall catalyst performance in the cyclic process is governed by the behavior of the catalyst in all of the significant reactions which occur during the cycle, together with the change in catalyst temperature over the course of a cycle. The rates of one or more of these reactions may be controlling for a selected cycle so that the process is not singularly dependent on reaction (1) as in the case of continuous reforming.

To determine the extent to which the overall catalyst performance in cyclic operation differs from continuous reforming, a series of cyclic tests were made in the laboratory reforming apparatus at reactor tube wall temperatures from 1400°F. to 1900°F. (Table 1). The catalyst samples used were first determined to have approximately equal activity for continuous reforming at a set of standard activity test conditions in the same apparatus (see Table 2). The cycle simulated conditions for a process presently under development at the Institute.[28] After each cyclic test, the activity of the catalyst was again checked at continuous conditions to ascertain that no permanent change in the catalyst had occurred during the course of the tests. Overall catalyst performance is illustrated by Figure 2, in which the percentage of hydrocarbon conversion is plotted against reactor tube wall temperature. It can be seen that although the activity of all of the catalyst samples was considered equivalent for the continuous process, under cyclic conditions their performance differed widely. Not only were the levels of hydrocarbon conversion different for each catalyst, but the effect of temperature on conversion varied significantly for the different catalysts.

Several general characteristics of catalyst behavior under cyclic conditions can be observed from the data in Table 1 and Figure 2. The magnesia-supported catalysts used in this study were less effective for cyclic reforming than were the alumina-supported catalysts. Not only did the magnesia-supported catalysts (curves C(b) and D, Figure 2) give lower conversion at equivalent temperature and natural gas feed space velocity than did the alumina supported catalysts (curves A and B), but the decrease in conversion with reduction in temperature was also much more severe.

There was also considerable evidence that the portion of nickel entering into oxidation and reduction reactions during the cycle was greater for the alumina supported catalysts. This was indicated by the catalyst temperature, carbon dioxide-carbon monoxide ratio in the product gas, and agreement between the quantities of water decomposition calculated from hydrogen and oxygen balances. In several instances with the alumina-supported catalyst, especially at high reactor temperatures (see Runs 19, 20, 28 and 29, Table 1), the catalyst bed temperature approached or exceeded the reactor tube wall temperature, indicating a sizable release of exothermic reaction heat from oxidation of metallic nickel. In these same instances, the ratio of carbon dioxide to carbon monoxide in the product gas was considerably higher than the carbon oxides ratio normally resulting from water-gas shift reaction (2). This is due to carbon dioxide formation at the beginning of the cycle by reaction (4) in which nickel oxide is reduced to metallic nickel. The quantity of water decomposition for the process calculated from both hydrogen and oxygen balances should agree if only reactions (1) and (2) were significant. In the runs where oxygen was transferred by the catalyst, the calculated quantity of steam decomposition based on a hydrogen balance appears lower than actual. Conversely, the oxygen content of carbon dioxide formed by reaction (4) will make the calculated quantity of steam decomposition based on an oxygen balance appear higher than actual. These observations in

Table 1.-RESULTS OF CYCLIC REFORMING TESTS IN LABORATORY REFORMING UNIT

Catalyst Designation	A			B		C							D		
Test No.	18	19	20	28	29	14	13	15	10	12	16	17	21	22	23
Catalyst, IGT Sample No.	3624	--	3931	4023	--	--	--	--	3623	--	--	3789	3764	--	3788
Promoter		MgO		None					None					None	
Support Material and Nominal Size	1" Alumina			1" Alumina		1" Magnesia							1" Magnesia		
Total Acid Soluble Nickel, wt. %	5.14	--	4.14	4.48	--	--	--	--	4.99	--	--	4.07	5.16	--	4.64
Condition	New	Used[a]	Used[a]	New	Used[a]	Used[a]	Used[a]	Used[a]	New	Used[a]	Used[a]	Used[a]	New	Used[a]	Used[a]
Operating Conditions															
Cycle Duration, sec.	480														
Natural Gas Feed, %	20														
Air Feed, %	60														
N_2 Purge, %	20														
Reactor Pressure, inches Hg	29.48	29.98	29.94	30.04	29.87	29.11	29.58	30.31	29.80	29.19	29.57	30.13	29.73	29.50	29.13
Reactor Tube Wall Temperature, °F.	1500	1700	1900	1700	1500	1500	1500	1700	1700	1700	1900	1900	1700	1500	1400
Catalyst Bed Height, inches	24	24	24	24	24	24	24	24	24	24	24	24	24	24	24
Volume, cu.ft.	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Temperature, °F., Top	1365	1597	1875	1594	1396	1390	1390	1555	1540	1540	1790	1725	1598	1417	1321
Middle	1460	1695	1940	1776	1515	1450	1450	1645	1620	1605	1865	1835	1653	1462	1361
Bottom	1440	1668	1860	1685	1501	1420	1430	1610	1620	1600	1790	1810	1620	1445	1347
Steam Feed, lb./cu.ft. catalyst-hr.	55.3	58.6	52.2	54.6	56.2	34.0	51.6	33.1	58.4	52.5	32.1	56.1	61.8	51.1	51.3
Steam/Natural Gas Mole Ratio	2.24	2.34	2.09	2.14	2.26	2.20	2.10	2.02	2.27	2.09	1.99	2.19	2.50	2.09	2.11
Steam/Carbon Mole Ratio	2.08	2.17	1.94	2.02	2.12	2.04	1.95	1.88	2.18	2.01	1.86	2.03	2.36	1.98	2.00
Natural Gas Feed, SCF/cu.ft. catalyst-hr.	528	536	534	546	531	331	527	344	540	536	345	547	529	521	520
Air Feed, SCF/cu.ft. catalyst-hr.	4089	4173	4160	4170	4347	4091	4141	4205	4333	4086	4108	4196	4141	4118	3947
N_2 Feed, SCF/cu.ft. catalyst-hr.	1420	1448	1430	1419	1429	1427	1471	1466	1475	1437	1430	1462	1427	1474	1408
Operating Results[b]															
Space Time Yield, SCF/cu.ft. catalyst-hr.	2238	2263	1778	1795	1771	624	556	1381	2243	2145	1330	2223	2291	2060	1403
Expansion, SCF prod. gas/SCF feed gas	4.24	4.22	3.33	3.29	3.33	1.86	1.06	4.01	4.16	4.00	3.86	4.06	4.33	3.95	2.70
Steam Decomposition, mole/mole feed gas															
Calculated from Hydrogen Balance	1.239	1.017	0.209	0.220	0.256	0.381	-0.210	1.031	1.313	1.123	0.744	0.964	1.298	1.275	0.606
Calculated from Oxygen Balance	1.350	1.574	1.534	1.527	1.679	0.388	0.124	1.271	1.193	1.175	1.367	1.320	1.301	1.698	0.862
Carbon Balance, %	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Hydrocarbon Conversion[c], %	93.5	98.0	99.2	98.7	96.1	22.6	11.1	92.8	88.1	89.7	99.0	98.1	94.4	77.5	57.2
Product Gas Properties[d]															
Composition, mole %															
Hydrogen	73.9	71.2	66.7	66.1	65.6	40.5	3.3	72.5	74.0	73.0	71.2	72.7	74.2	71.5	60.7
Methane	1.6	0.5	0.3	0.4	1.2	44.5	75.3	1.9	3.0	2.7	0.3	0.5	0.7	5.3	15.3
Ethane	0.0	0.0	0.0	0.0	0.0	0.0	2.5	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.7
Other Hydrocarbons	0.0	0.0	0.0	0.0	0.0	0.0	4.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.6
Carbon Monoxide	15.4	17.5	17.7	16.6	13.3	5.1	10.7	17.8	15.2	17.0	19.5	19.2	17.0	15.2	11.9
Carbon Dioxide	8.4	10.1	14.4	15.1	18.7	8.3	1.3	7.1	6.9	6.3	8.2	6.9	6.7	6.4	8.6
Nitrogen	0.7	0.7	0.9	1.8	1.2	1.6	2.8	0.7	0.9	1.0	0.8	0.7	1.4	1.5	2.2
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Heating Value, B.t.u./SCF	301	288	272	268	263	589	918	307	314	314	292	298	297	331	411
Specific Gravity, Air = 1	0.344	0.320	0.448	0.457	0.478	0.467	0.645	0.348	0.329	0.336	0.373	0.351	0.336	0.340	0.412
Natural Gas Properties[d]															
Composition, mole %															
Methane	88.5	88.5	88.5	85.1	85.1	88.5	88.5	88.5	88.5	88.5	88.5	88.5	85.1	85.1	85.1
Ethane	5.0	5.0	5.0	5.3	5.3	5.0	5.0	5.0	4.7	4.7	5.0	5.0	5.3	5.3	5.3
Propane	1.9	1.9	1.9	2.1	2.1	1.9	1.9	1.9	1.7	1.7	1.9	1.9	2.1	2.1	2.1
Butane	0.51	0.51	0.51	0.62	0.62	0.51	0.51	0.51	0.50	0.50	0.51	0.51	0.62	0.62	0.62
Pentane	0.07	0.07	0.07	0.05	0.05	0.07	0.07	0.07	0.05	0.05	0.07	0.07	0.05	0.05	0.05
Hexane	0.04	0.04	0.04	0.03	0.03	0.04	0.04	0.04	0.03	0.03	0.04	0.04	0.03	0.03	0.03
Heptane	0.02	0.02	0.02	0.01	0.01	0.02	0.02	0.02	0.01	0.01	0.02	0.02	0.01	0.01	0.01
Carbon Dioxide	0.75	0.75	0.75	0.66	0.66	0.75	0.75	0.75	0.67	0.67	0.75	0.75	0.66	0.66	0.66
Helium	0.16	0.16	0.16	0.23	0.23	0.16	0.16	0.16	0.00	0.00	0.16	0.16	0.23	0.23	0.23
Nitrogen	3.0	3.0	3.0	5.9	5.9	3.0	3.0	3.0	3.8	3.8	3.0	3.0	5.9	5.9	5.9
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Heating Value, B.t.u./SCF	1039	1039	1039	1018	1018	1039	1039	1039	1033	1033	1039	1039	1018	1018	1018
Specific Gravity, Air = 1	0.627	0.627	0.627	0.643	0.643	0.627	0.627	0.627	0.626	0.626	0.627	0.627	0.643	0.643	0.643

[a] The same catalyst sample was used for tests 10 through 17. The same catalyst sample was used for tests 18, 19 and 20. The same catalyst sample was used for tests 21, 22 and 23. The same catalyst sample was used for tests 28 and 29. Preceeding each test the catalyst was first burned off with air for approximately 30 minutes at 1700°F. tube wall temperature and then checked for activity under continuous reforming conditions at 700 SCF/cu.ft. catalyst-hr. natural gas space velocity and 1700°F. tube wall temperature. In each case the activity was equivalent to that of the new catalyst.

[b] Operating results for cyclic operation are based on product gas volumes calculated from the feed gas and product gas compositions assuming 100% carbon balance.

[c] Percentage disappearance of carbon (as hydrocarbon) from the feed gas.

[d] Mass spectrometer analysis.

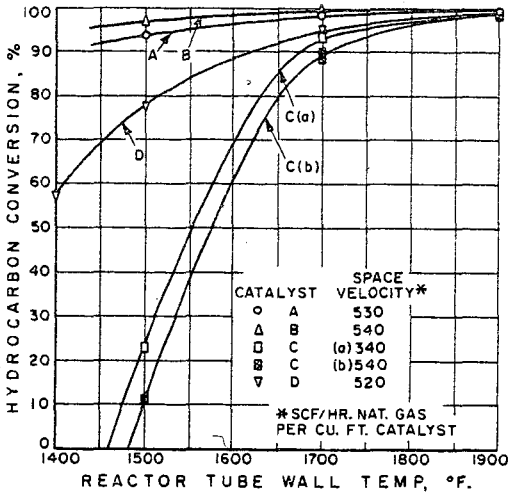

Fig. 2.-COMPARISON OF REFORMING CATALYST PERFORMANCE IN CYCLIC LABORATORY OPERATION

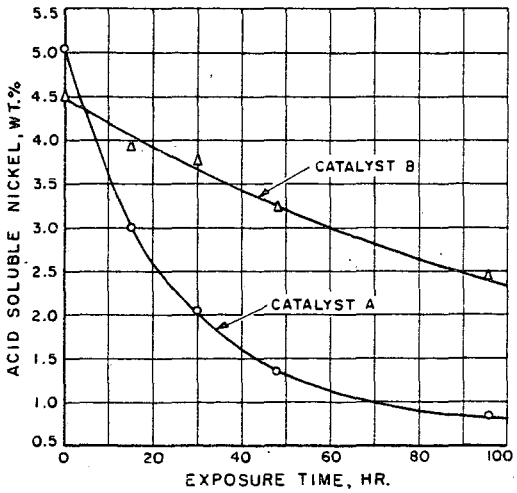

Fig. 3.-DECREASE IN CONCENTRATION OF ACID SOLUBLE NICKEL IN ALUMINA SUPPORTED CATALYSTS ON EXPOSURE AT 1800°F IN AIR

the case of the alumina-supported catalyst seem to indicate higher rates of oxidation and reduction of nickel than occurred with the magnesia-supported catalyst.

It can also be noted that the general level of hydrocarbon conversion and the apparent quantities of nickel cyclically undergoing oxidation and reduction were higher for the high purity, unpromoted alumina-base catalyst (B) than for the lower purity alumina-supported, magnesia-promoted catalyst (A). It is not possible to draw conclusions regarding the effect of base impurities and promoter from these data, however.

Overall catalyst performance as shown in Figure 2 does not indicate the specific effect of individual catalyst properties, but rather reflects the cumulative effect of the complex factors influencing cyclic reforming operation which are not readily apparent from characteristics of the catalyst under continuous reforming conditions. One might conclude from these data that high catalyst performance under cyclic conditions is closely related to the susceptibility of the catalyst to oxidation and reduction of its nickel content. This conclusion would seem logical, since it is evident that the steam-hydrocarbon reaction (1) is primarily dependent upon the presence of some form of metallic nickel as the catalytic agent.

Recent work in the field of solid state physics dealing with the relationships between the electronic properties of semiconductor metal oxides and their catalytic behavior has shed additional light on the factors which influence the oxidation and reduction reactions of nickel.[4,10,12,36,37,45,46,47] These factors can be summarized as follows:

a) Source of nickel oxide. Nickel oxide prepared from different nickel salts can differ significantly in chemical properties.[2,27]
b) Treatment of nickel oxide. Temperature, pressure and atmospheric exposure have been demonstrated experimentally to change the susceptibility of nickel oxide to reduction by hydrogen.[2,9,18,27] It has been found that the combination, sequence, duration and rate of change of treatment conditions are all important in determining its behavior during subsequent reduction.[18] Thus the treatment of nickel oxide during preparation of the catalyst, and the treatment received in operation in the cyclic process, are both important in determining its behavior.
c) Promoters or impurities in the nickel oxide. Studies have shown that the inclusion of foreign metal ions in the crystal lattice of nickel oxide has a pronounced effect on its chemical reactivity, including reduction to metallic nickel.[8,19,37]
d) Support material. The susceptibility of nickel oxide to reduction by hydrogen is influenced by the electronic nature of an adjacent material, even though there is no chemical reaction or solid solution between the two materials.[14,38,39]

It should be noted that the foregoing factors are all related to changes in, or variations of, the crystal structure of nickel oxide. Present-day considerations in the manufacture of supported nickel reforming catalysts include nickel concentration and distribution, support porosity, surface area and the mechanical properties of the support. The selection of promoters is based largely on initial activity considerations. Little attention, however, is given to

Table 2.-RESULTS OF STANDARD CATALYST ACTIVITY TESTS IN LABORATORY REFORMING UNIT

Catalyst Designation	A			B	C			D		
Test No.	4	5	6	27	1	2	3	7	9	8
Catalyst, IGT Sample No.	3624	--	3672	4023	3623	--	3635	3664	3665	3666
Promoter		MgO		None		None			None	
Support Material and Nominal Size		1" Alumina		1" Alumina		1" Magnesia			1" Magnesia	
Total Acid Soluble Nickel, wt. %	5.14	--	4.08	4.48	4.99	--	4.63	4.47	4.01	3.69
Condition	New	Oxidized[a]	Oxidized[b]	New	New	Oxidized[c]	Oxidized[d]	Used[e]	Used[e]	Used[e]
Operating Conditions										
Reactor Pressure, inches Hg	30.46	30.83	30.10	29.36	30.61	30.50	30.15	30.37	29.77	29.42
Reactor Tube Wall Temperature, °F.	1700	1700	1700	1700	1700	1700	1700	1700	1700	1700
Catalyst Bed Height, inches	24	24	24	24	24	24	24	24	24	24
Volume, cu.ft.	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Temperature, °F., Top	1450	1448	1397	1392	1459	1433	1496	1414	1603	1648
Middle	1515	1471	1425	1460	1459	1433	1520	1395	1605	1665
Bottom	1315	1254	1454	1544	1528	1514	1477	1511	1455	1491
Steam Feed, lb./cu.ft. catalyst-hr.	79.2	52.5	52.5	53.5	63.3	58.7	40.6	80.9	22.5	45.6
Steam/Natural Gas Mole Ratio	2.49	1.68	1.88	1.77	1.89	1.64	1.76	1.92	2.23	8.67
Steam/Carbon Mole Ratio	2.34	1.58	1.77	1.68	1.77	1.54	1.65	1.80	2.10	8.16
Natural Gas Feed, SCF/cu.ft. catalyst-hr.	669	656	587	645	715	764	494	903	216	113
Operating Results										
Space Time Yield, SCF/cu.ft. catalyst-hr.	2410	2464	2269	2071	2535	2711	1711	3278	634	163
Expansion, SCF prod. gas/SCF feed gas	3.60	3.75	3.87	3.21	3.55	3.55	3.46	3.63	2.93	1.45
Carbon Balance, %	96.0	103.2	104.1	89.3	92.3	95.0	92.2	104.4	98.4	98.8
Steam Decomposition, mole/mole feed gas										
Calculated from Hydrogen Balance	1.055	1.148	1.181	0.734	1.015	0.997	1.021	0.903	0.821	0.199
Calculated from Oxygen Balance	0.996	0.896	1.053	0.889	0.883	0.893	0.767	1.022	0.764	0.163
Hydrocarbon Conversion,[f] %	74.4	73.6	76.9	75.6	74.7	73.3	70.9	70.3	44.3	10.2
Product Gas Properties										
Composition, mole %[g]										
Hydrogen	69.8	69.7	70.3	69.0	69.9	68.6	69.5	68.8	62.9	25.7
Methane	7.6	7.4	6.3	7.7	7.6	8.0	8.9	8.2	16.8	60.9
Ethane	0.0	0.0	0.0	0.2	0.0	0.0	0.0	0.2	0.0	0.1
Other Hydrocarbons	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	2.3
Carbon Monoxide	14.1	17.2	16.9	14.6	15.5	16.0	16.3	15.4	11.1	1.0
Carbon Dioxide	6.9	4.6	5.4	6.7	4.7	4.6	3.1	6.6	7.7	5.6
Nitrogen	1.6	1.1	1.1	1.8	2.3	2.8	2.2	0.8	1.5	4.4
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Heating Value, B.t.u./SCF	343	351	341	347	348	349	362	354	403	731
Specific Gravity, Air = 1	0.349	0.337	0.341	0.354	0.335	0.344	0.324	0.353	0.378	0.517
Natural Gas Properties										
Composition, mole %[g]										
Methane	86.8	89.8	89.8	86.8	86.1	86.1	86.8	89.4	88.5	88.5
Ethane	4.9	4.5	4.5	5.1	4.9	4.9	4.9	4.5	4.7	4.7
Propane	2.0	1.5	1.5	1.9	2.4	2.4	2.0	1.6	1.7	1.7
Butane	0.55	0.38	0.38	0.51	0.60	0.60	0.55	0.43	0.50	0.50
Pentane	0.08	0.05	0.05	0.04	0.09	0.09	0.08	0.06	0.05	0.05
Hexane	0.04	0.04	0.04	0.02	0.05	0.05	0.04	0.05	0.03	0.03
Heptane	0.01	0.01	0.01	0.01	0.02	0.02	0.01	0.02	0.01	0.01
Octane	0.02	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.00	0.00
Carbon Dioxide	0.60	0.90	0.90	0.56	0.42	0.42	0.60	0.72	0.67	0.67
Helium	0.14	0.12	0.12	0.18	0.20	0.20	0.14	0.07	0.00	0.00
Nitrogen	4.9	2.7	2.7	4.9	5.2	5.2	4.9	3.1	3.8	3.8
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Heating Value, B.t.u./SCF	1027	1029	1029	1021	1033	1033	1027	1031	1033	1033
Specific Gravity, Air = 1	0.636	0.619	0.619	0.633	0.640	0.640	0.636	0.622	0.626	0.626

[a] Oxidized in reactor tube with air at 1700°F. tube wall temperature for 6.5 hours following test No. 4.

[b] Oxidized in reactor tube with air at 1900°F. tube wall temperature for 5.75 hours following test No. 5.

[c] Oxidized in reactor tube with air at 1700°F. tube wall temperature for 4 hours following test No. 1.

[d] Oxidized in reactor tube with air at 1900°F. tube wall temperature for 5.5 hours following test No. 2.

[e] Removed from catalyst bed in cyclic pilot plant after approximately 29 hours of operation. Samples 3664, 3665 and 3666 are from top, middle and bottom of the bed, respectively.

[f] Percentage disappearance of carbon (as hydrocarbon) from feed gas.

[g] Mass spectrometer analysis.

conditions controlling the crystal structure of the nickel and nickel oxide. In view of the significance of the oxidation-reduction reactions in the cyclic process, these factors should not be overlooked. A combined effort is presently under way by members of the utility gas industry, equipment constructors and catalyst manufactures to develop suitable standards for catalyst specifications and to improve the performance and life of the catalyst. In this connection Milbourne has recently suggested an oxidation rate determination test as a method of evaluating cyclic reforming catalysts.[25] This approach seems to have merit in view of the data shown here.

PERMANENT LOSS OF CATALYST ACTIVITY

In the continuous reforming process the catalyst, as long as it is not poisoned by sulfur or similar impurities in the feed stream, apparently has unlimited life. Since this has not been the case in commercial operation of the cyclic reforming process it was suspected that loss of catalyst activity in cyclic use was related to the operating differences in the two processes already cited. These are cyclic variation in atmosphere and catalyst temperature which are not encountered in continuous reforming. All types of catalyst employed in the cyclic process have been subject to permanent loss in activity, although not necessarily at the same rate. For example, 1-inch diameter alumina-base promoted catalyst, and 1-inch diameter magnesia-base unpromoted catalyst have been observed to lose a major part of their activity after 2000 to 4000 hours of operation. On the other hand, some 1/2-inch alumina base unpromoted catalyst has been reported to have given essentially constant performance for about 20,000 hours.[25]

Effect of Oxygen

Since the atmosphere in the continuous reforming process is always reducing, an investigation was made of the effect of an oxidizing atmosphere on the catalyst. A series of tests was made in the laboratory reforming apparatus with both magnesia-supported and alumina-supported catalyst. Each catalyst was treated for 4 to 6.5 hours in a stream of air at 1700° and 1900°F. reactor tube wall temperature. Before and after each exposure, an activity test was made at comparable continuous reforming conditions. Results of these tests are shown in Table 2.

With the alumina-supported catalyst (A, Tests 4, 5 and 6), little change in reforming activity was observed even after exposure at 1900°F. Chemical analysis of the catalyst following final exposure indicated a nitric acid soluble nickel concentration of 4.08 weight per cent, compared to 5.14 weight per cent before exposure. An x-ray diffraction pattern of the catalyst after exposure contained lines corresponding to nickel aluminate (spinel) which were not present in the pattern of the new catalyst. It appeared that some of the nickel content of the catalyst had formed an insoluble spinel compound with the support material during the period of exposure, but that the reduction in concentration of available nickel was not sufficient to significantly affect the reforming activity.

With the magnesia-supported catalyst (C, Tests 1, 2 and 3), no reduction in reforming activity was observed after exposure at 1700°F., but following exposure at 1900°F. the reforming activity was approximately 2/3 that of the original catalyst. Chemical analysis indicated a nitric acid soluble nickel concentration of 4.63 weight per cent following final exposure compared to 4.99 weight per cent in the new catalyst. The x-ray diffraction pattern of the exposed catalyst

contained only lines corresponding to periclase (MgO). With the magnesia-supported catalyst, exposure in air at elevated temperature had a more serious effect on reforming activity than in the case of the alumina-supported catalyst, although the reduction in nitric acid soluble nickel content was less, and no compound formation was detected for the magnesia catalyst. An examination of the phase diagram for the nickel oxide-magnesium oxide system[23,24] does not indicate the existence of a compound; however, Holgersson and Karlsson confirmed the existence of a completely miscible system of solid solutions between these two materials.[15] Since both nickel oxide and magnesium oxide have face-centered cubic lattices with nearly the same unit cell length, low concentrations of solid solution, if present, would probably not be detectable in the x-ray diffraction pattern.

Although the specific relation between catalyst changes and reforming activity was not defined in these tests, the indications fit the circumstances. In the case of the alumina-supported catalyst, combination of the nickel content with the alumina support to form spinel would be expected to reduce reforming activity, since spinel compounds are very unreactive, and reduction to metallic nickel with hydrogen or hydrocarbons would be unlikely. In the case of the magnesia-supported catalyst, solution of the nickel content in the unreactive magnesium oxide lattice could easily make the nickel unavailable for reduction by hydrogen or hydrocarbons. Both cases would be unique to the cyclic reforming process, since either would proceed only with nickel present as nickel oxide.

Spinel

Additional tests were conducted to determine if the rate of spinel formation was rapid enough to contribute materially to loss of catalyst activity at conditions of the cyclic reforming process. Samples of both the high purity alumina-base unpromoted catalyst (B), and the lower purity alumina-base magnesia-promoted catalyst (A), were crushed to pass 100 mesh. Each catalyst was heated to 1800°F. in an electric furnace for an extended period in contact with air. At intervals, samples were withdrawn for determination of nitric acid soluble nickel concentration. The change in nitric acid soluble nickel content with time of exposure is shown in Figure 3.

After 96 hours at the test conditions both catalysts showed a marked decrease in the concentration of acid soluble nickel. It is interesting to note the difference in rate of decrease for these two catalysts. In curve B for the high-purity alumina support the rate of decrease was almost a linear function of time. Since only nickel oxide and alumina were present in this catalyst, nickel aluminate would be the only suspected compound which would lower the concentration of acid soluble nickel. This was confirmed by the x-ray diffraction pattern of the catalyst after exposure for 96 hours. Only lines corresponding to α-alumina, nickel oxide and spinel were detected. No spinel lines were observed in the pattern for the new catalyst. Curve A for the lower purity alumina base catalyst shows a different time-nickel concentration relationship. The decrease in acid soluble nickel content was very rapid initially, but approached the rate in curve B after about 30 hours. The major materials present in this catalyst in addition to alumina and nickel oxide were 12.90 weight per cent silica in the support, and 1.8 weight per cent magnesia added as promoter by coimpregnation as nitrate with the nickel. An x-ray diffraction pattern of this catalyst indicated that the silica was in the form of aluminum silicate ($3Al_2O_3 \cdot 2SiO_2$). In addition to spinel lines, the pattern of the catalyst after 96 hours of exposure contained unidentified lines corresponding to 5.4, 4.7 and 1.84A. These do

not correspond to any nickel compound for which x-ray data are readily available. The difference between curves A and B could be attributed either to the formation of insoluble nickel compounds in addition to nickel aluminate, or to an increased rate of formation of nickel aluminate due to the presence of silica or magnesia.

Solid Solutions

To determine the relationship between catalyst activity and the possible formation of solid solutions between nickel oxide and the magnesia catalyst support as indicated by the atmosphere tests described above, a number of samples of the same magnesia-supported catalyst C having various operating histories and showing different levels of activity under comparable continuous reforming conditions were subjected to microscopic analysis. Descriptive data for the samples selected are itemized below:

IGT Sample No.	3623	3664	3635	3665
Acid Soluble Nickel, wt. %	4.99	4.47	4.63	4.01
Approximate Relative Continuous Reforming Activity, %	100	120	70	15
History	New	29 hours Pilot Plant Operation at 1400-1660°F.	Oxidized in Tube Furnace for 9.5 hours at 1700-1900° F.	29 hours Pilot Plant Operatic at 1830-1890°F.

For each sample the catalyst pellet was impregnated with Canada balsam, after which a thin section through the center was prepared. Photographs of the sections made with transmitted light are shown in Figures 4, 5, 6 and 7. The original pore structure of the support material was preserved and shows as white areas in these photographs.

In Figure 4, the new catalyst, two distinct phases are apparent; a colorless isotropic phase having an index of refraction slightly below that of a 1.74 immersion medium (refractive index of periclase: 1.734-1.737) and a black opaque phase (nickel oxide). The nickel oxide is concentrated near the surface of the pellet and especially around the perimeter of the larger pores. Particle size of the periclase ranged from a maximum of approximately 50 microns down to a very fine dust. The nickel oxide particle size wastoo small to be determined.

Figure 5 shows a section of the catalyst after brief cyclic operation in a pilot plant at relatively low temperature. The activity under continuous reforming conditions in the laboratory apparatus was found to be noticeably higher than that of the new catalyst. Two phases are apparent, as in the new catalyst. However, the nickel oxide seems to be more uniformly distributed throughout the pellet, and instead of being concentrated around the pore perimeters it appears to have diffused into a thin layer in the grain boundary surrounding each periclase crystallite. Some grains have a refractive index slightly above 1.74, whereas others have a refractive index lower than 1.74. Since nickel oxide has a refractive index of 2.37, the grains with a refractive index higher than 1.74 undoubtedly contain nickel oxide in solid solution. Solid solution formation in this sample is evidently in initial stages and far from complete.

Figure 6 shows a section of the catalyst following air treatment in the laboratory reforming apparatus at 1900°F. reactor tube wall

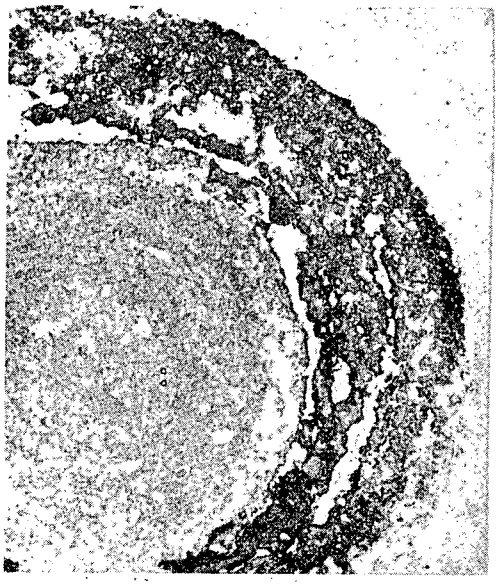

Fig. 4.-NEW CATALYST C,
RELATIVE ACTIVITY = 100%

Fig. 5.-USED CATALYST C,
RELATIVE ACTIVITY = 120%

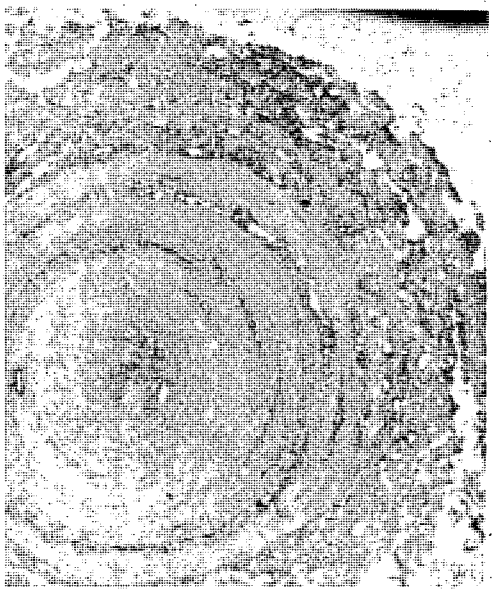

Fig. 6.-TREATED CATALYST C,
RELATIVE ACTIVITY = 70%

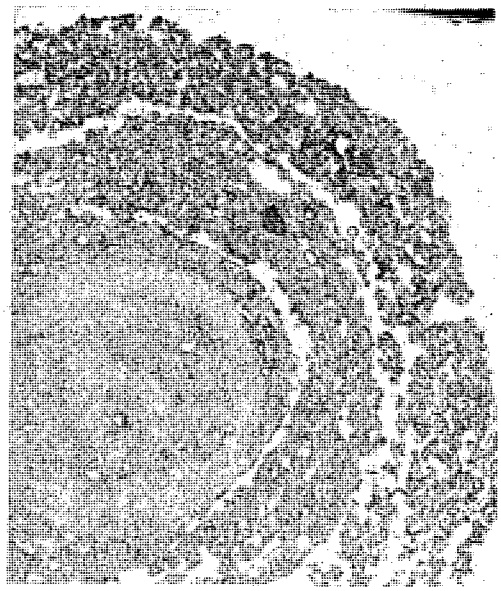

Fig. 7.-USED CATALYST C,
RELATIVE ACTIVITY = 15%

temperature (Test 3, Table 2). This sample was found to have approximately 2/3 of the activity of the new catalyst. Two phases can be detected in this sample, although the amount of black opaque phase has greatly diminished. Only a few grains were observed with an index of refraction less than 1.74, indicating a substantial amount of solid solution formation.

Figure 7 shows a sample of catalyst which was subjected to high temperatures in cyclic pilot plant operation. The activity of this material under continuous reforming conditions was very low, estimated at about 15% of the new catalyst. Only one phase can be detected in this sample, the nickel oxide phase having completely disappeared. Refractive indices of all grains were well above 1.74, indicating that solid solution of the nickel oxide in magnesia was essentially complete. No grains with an index of refraction greater than 1.78 were observed, indicating that the solutions formed were always dilute in nickel oxide. The largest particle size in the sample was approximately four times that in the new catalyst, indicating that some recrystallization may have occurred.

This series of analyses seems to indicate the path of the change which occurs in the magnesia-supported catalyst with use. It is interesting to note that the early changes in structure corresponding to nickel oxide migration throughout the pellet, and incomplete solid solution formation, are accompanied by an increase in reforming activity rather than a decrease. This result agrees with the findings of Hüttig with mixtures of metal oxide catalyst.[17] Hüttig describes a series of states that occur during the formation of a solid solution from a mixture of metal oxides. The initial states constitute diffusion of the more mobile lattice over and around the less mobile lattice. Hüttig relates the highly disordered condition which is created to increased catalytic activity. The final state, constituting the complete solution and filling in of lattice defects, he relates to diminishing catalytic activity.

CONCLUSIONS

It appears from the results of this study that the factors which influence overall performance of the catalyst in the cyclic reforming process, as well as catalyst life, are quite different from significant factors for the continuous reforming process. For this reason, catalyst properties which have generally been considered desirable in continuous reforming catalysts may not be satisfactory for the cyclic process. Likewise, the methods commonly used to evaluate catalyst performance for continuous reforming do not appear adequate to predict the behavior of catalysts under cyclic conditions.

Although the cyclic process is extremely complex, the data from this study lead to several general conclusions regarding performance of supported nickel catalysts of the type employed in commercial practice. First, the susceptibility of the nickel content of the catalyst to rapid oxidation and reduction appears to be closely related to good overall reforming efficiency in cyclic operation. Second, catalyst activity is decreased by any changes which result in decreasing the amount of nickel available for oxidation and reduction. For alumina-supported catalysts a major factor contributing to loss in activity appears to be the formation of spinel by reaction between nickel oxide and the support. For magnesia-supported catalysts a similar effect appears to result from solution of nickel oxide in the support. In both instances, the undesirable changes must occur during the heating portion of the cycle, when all or part of the nickel is present as the oxide.

Many other factors may contribute to short catalyst life in the cyclic reforming process. One for which very little specific data are available is the effect of coatings built up on the surface of the catalyst with use, from dust constituents in the combustion air, or from ash content of oil feed or fuel. Additional studies will be necessary to define these effects, as well as to determine methods for improving catalyst performance and life.

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