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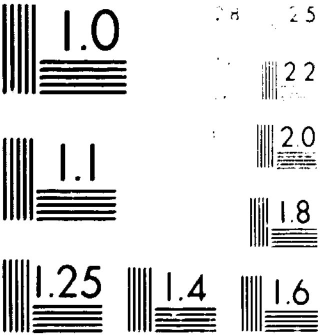
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APPLICATION OF STEAM GASEOUS HYDROCARBONS REFORMING CATALYST*

by

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ABSTRACT

The principle properties of three types Z-107, Z-204R and Z-204 catalysts developed successfully in the recent years for steam gaseous hydrocarbons reforming and their practical application in the ammonia plants with a capacity of 300-1000 tons ammonia per day are presented in this paper. Some data regarding the property changes of these catalysts in the use of ammonia plants are given.

Ferthermore, the volatilization of nickel contained in the reforming catalyst at high temperature area of the secondary reformer is briefly discussed. At the same time the research result of the steam reforming reaction kinetics of Z-107 is described.

We have begun developing reforming catalysts since 1959. The earlier developed catalyst was Type CN-1 extruded agglomerating nickel catalyst with alumina as carrier, which was used in the ammonia plants in the early 60's.

With the development of pressurized steam reforming process, we developed Type Z-102 reforming catalyst in mid 60's. It began to be put into commercial use in 1966 and up to now it has been extensively used in some ammonia plants with lower reforming pressures (less than 20 kg/cm^2 g) and hydrogen production plants.

In the 70's, because of the advancement of various gaseous hydrocarbons reforming processes and particularly for the requirement of the large scale ammonia plants, we developed successively Type Z-204, CN-5, CN-6, Z-107, CN-8 and Z-204R reforming catalysts, among which Z-107, Z-204 and Z-204R have been used in the large or middle scale ammonia plants. For the above described catalysts, some are cementing types and some are agglomerating types; some are formed by pressurization and some by extrution; they are pillar, Raschig ring or special shapes. For more than twenty years we have studied the effects of the reaction conditions for the manufacture of reforming catalyst, the types and dosages of cementing agents, the particle sizes of raw materials the temperatures and time for calcine etc. on the performence of catalysts. Also we have studied the reaction Kinetics. In addition to these, the changing rules of the reforming catalyst performance in the operation of industrial units have been surveyed.
All these helped us a lot in developing the reforming catalysts with good performance, recommending :

reliable application precedures on these catalysts and judging the remaining life of the reforming catalysts used in the commercial reforming furnaces.

Based on the study of manufacturing conditions, performances and reliable application procedures, Type Z-107, Z-204R and Z-204 have successfully been put into practical use in the large (1000 t/d ammonia) and middle scale (less than 300 t/d ammonia) ammonia plants.

PRIMARY REFORMING CATALYST

Type Z-107 catalyst is a primary reforming catalyst recommended to be used in the large or middle scale ammonia plants. It is agglomerating type catalyst with $-Al_2O_3$ as carrier, which has the main properties shown in Table 1.

Z-107 catalyst consists of both longer and shorter rings. They are normally used in conjunction with each other and possess the similar chemical composition and physical-chemical parameters.

We chose the suitable particle sizes of raw materials and calcine conditions when manufacturing Z-107 catalyst, hence making its structure more stable, the strength less decrease, the active composition unapt to interreact with the carrier during the operation. Table 2 shows the operating variables of Z-107 catalyst used in the primary reformer of the large scale ammonia plants.

Table 1. Principle Properties of Type Z-107 Catalyst

Size (mm) & Shape	Side Crush Strength (kg/granula)	Bulk Density (kg/litre)	Chemical Composition (%)				
			Al_2O_3	NiO	SiO	K+Na	S
Ø 16x16x6 (ring)	40	1.19	84	12-16	0.20	0.20	trace
Ø 16x8x6 (ring)	25	1.22	84	12-16	0.20	0.20	trace

Table 2. Performance Comparison of a Few Catalyst Used In the Primary Reformer of a Ammonia plant with a capacity of 1000 Y/D

Catalyst	Load (%)	Outlet Pre. (kg/cm^2)	Reforming Tube Resistance (kg/cm^2)	Water/ Carbon Ratio	Tube wall Temp. (°C)	Outlet Temp. (°C)	CH_4 in Reformed gas (%)	Tempereture Approach to Equiliorium (°C)
Design Figure	100	31.6	3.6	3.54	930	822	9.60	11-27.5
Z-107	100	31	3-3.5	3.48	870	785	10.15	-2.2 x
A1 xx	100	31	3-3.5	3.55	880	788	9.97	-2.3
A2 xx	100	31	3-3.5	3.72	880	794	11.8	21.5

Notes: x The operation result taken from the first half year

xx A1 & A2 are the similar commercial catalysts on the international market.

It is shown from the half year operation result of a ammonia plant with a capacity of 1000 T/D ammonia listed in Table 2 that for Z-107 catalyst there is an outlet temperature of -2.2 °C approach to the equilibrium, it is not only far less than the process design requirement of 11 °C temperature approach to equilibrium for the new catalyst, but also with a good activity compared with the other commercial catalysts on the international market. At the same time it has been found that the tube wall temperatures are even during the operation and the working condition is normal. The application of Z-107 catalyst illustrates the following features:

1) Easy Reduction: The reduction property of the primary reforming catalyst will directly affect the normal operation of the unit. Especially, the lower temperature existed in the tube inlet area and the higher steam partial pressure are unfavorable to the reduction of reforming catalyst, but the change of these conditions are limited by the process and equipment. If the catalyst has no good reduction property it can not be completely reduced at the above-said area and its excellent activity can not be brought into full play in the commercial reformers. In the serious cases " hot band" will occur in the tubes, which will shorten the tube life and will interrupt the normal operation of the system.

When Z-107 catalyst is reduced with hydrogen containing gas, it starts to reduce at 300 °C - 310 °C and completes 100 % reduction at 420 °C. When Z-1o7 catalyst is used in the large scale ammonia plant, only after ten minutes or more from the beginning of reduction operation at 700 °C - 760 °C it is clearly found that the endothermic reaction within the tubes is drastically carrying out, the tube wall temperature is decreased, and the methane content in the reformed gas is quickly cut down to approach to the equilibrium value. Although the oxidation atomosphere of high temperature and higher steam partial pressure exists in the tubes during the emergency shut down period, the catalyst can still be thoroughly reduced quickly after the restart up of the unit.

The analytical result of Z-107 catalyst after being used in the large scale ammonia plant under the precess conditions shows that the reducible nickel still amounts to more than 90 % of the total nickel. It is known that there has been less combination between the active nickel and Al_2O_3 carrier.

2) Stable Strength: In the past, the strength decline of the primary reforming catalysts during the operation of industrial units would usually force the whole unit to shut down for replacing catalysts.(1) But it is seen from Table 3 that the strength decline of the used Z-107 is just a little and it is still far more than the requirement of 10-13 kg/cm^2 above which the side crush strength of the primary reforming catalyst in the large scale ammonia plant should be.(2)

Table 3 Strength of Type Z-107 Catalyst After the Industrial Operation

Side Crush Strength of Z-107 Catalyst Along the Length of Tubes (kg/granula)

1m	2m	3m	4m	5m	6m	7m	8m	9m	10m
26.8	25.5	26.2	29.7	34.5	59.3	60.4	66.2	56.9	58.6

Therefore, the pressure drop of the tubes in the operation of the ammonia plant using Z-107 catalyst is stable, ensuring a well-distributed gas stream between the tubes of the furnace and a uniform tube wall temperature.

3) Less detrimental Impurities: It is well known that many impurities may affect the activity and heat resistivity of the reforming catalyst and some may affect the operation of the down stream units in the ammonia plant.(3,4) When Z-107 catalyst is manufactured, on one hand the raw materials with high purity are selected, on the other hand some effective measures are taken to strictly avoid the entering of the impurities. Therefore Z-107 catalyst just contains a little impurities, for example,

Impurities	SiO_2	K+Na	Fe_2O_3	S	Cl	P	As	Pb
Content: (%)	0.20	0.20	0.20	trace				

In the course of the heat-up reduction in the industrial unit using Z-107 catalyst, the content of H_2S in the effluent gas is less than 0.5 ppm from start to finish. There have been no silicon, sodium and potasium migration existed to harmfully affect the down stream systems in the operation.

4) Stable Activity: A large number of observations on the structure of the primary reforming catalyst used in the industrial furnaces demonstrates that the reforming catalyst is continuing to sinter obviously when being used.(5) It can be seen from Table 4 that although Z-107 catalyst is without exception, its structure changes slightly as compared with the other commercial catalysts widely sold on the international market.

Table 4. Changes of Physical-Chemical Parameters for the Primary Reforming Catalysts

Catalyst Designation	Before or After use	False Density (kg.cm^3)	Specific Surface Area(m^2/g)	Pore Volume (cm^3/g)	Average Pore Radius (A^o)
Z-107	before	2.50	5.70	0.147	516
	after	2.23	2.46	0.238	1935
A1^x	before	2.64	5.20	0.148	546
	after	2.34	2.41	0.188	1030
A2^x	before	2.20	116	0.172	32
	after	1.82	2.4	0.382	3180

Note : x A1 & A2 are the primary reforming catalyst sold extensively on the international market.

When studying on the changes of the physical-chemical parameters for the primary reforming catalyst along the length of the tube, the results show that the changes of various properties along the tube length correspond with the trend of Figure 1. The range of decreasing the specific surface area increases uninterruptedly from top to bottom of the tubes, but almost ceases below 3-4 meters from the upper end of tubes. Obviously, this closely relates to the gas composition and temperature at the various heights inside the tubes.

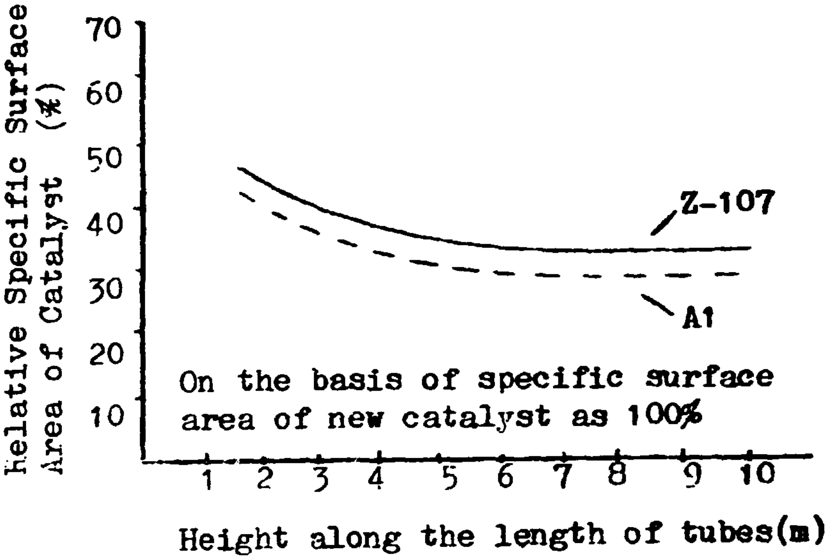

Figure 1. Changes of Catalyst Specific Surface Area Along the Length of the Tubes Under the Process Conditions of the Large scale Ammonia Plant

All research results indicate that the continued sinter of the reforming catalysts in the course of use is one of the important reasons causing the activity decline. The activity decline of the various catalysts during the initial period of use is faster. Hence to lay stress on studying the decreasing rate of the catalyst activity during the initial time of use is essential. Only the activity which is at a period of stable activity has a practial meaning in industrial operation. We have studied on the reaction kinetics of

Z-107 catalyst already used under the process conditions of the large scale ammonia plant (for about 8-10 months). The research was carried out at a pressure of 30 kg/cm^2 by using a catalyst of commercial size (i.e. complete granula).

The result showed that the rate equation of steam methane reforming reaction on Z-107 at 500-800 °C, under the pressure of 30 kg/cm^2 and a water to carbon ratio of 3.5-4.5 is:

$$W=Ae^{\frac{-E}{RT}} P_{CH_4} \cdot P_{H_2O} \cdot P_{H_2}^{-1}$$

Carbon monoxide is the one-step product of the reforming reaction. The apparent energy of activation of the complete granula Z-107 catalyst is 34.2 kcal/mol during the period of stable activity, while that of the commercial catalyst al similar to Z-107 Catalyst is 34-36 kcal/mol.

Figure 2 gives the performances of Catalysts Z-107, A1 and A2 used in the reformer of the same large scale ammonia plant.

Based on the above description it is known that the activity of Z-107 catalyst is stable.

Since Z-107 catalyst has features of easy reduction, more stable strength, less toxicants contained and stable activity, results of well-distributed and lower temperature of the tube wall in the primary reformer, stable pressure drop inside the tube and subsequently good quality of the reformed gas have been gained at a higher load in industrial units using Z-107 catalyst.

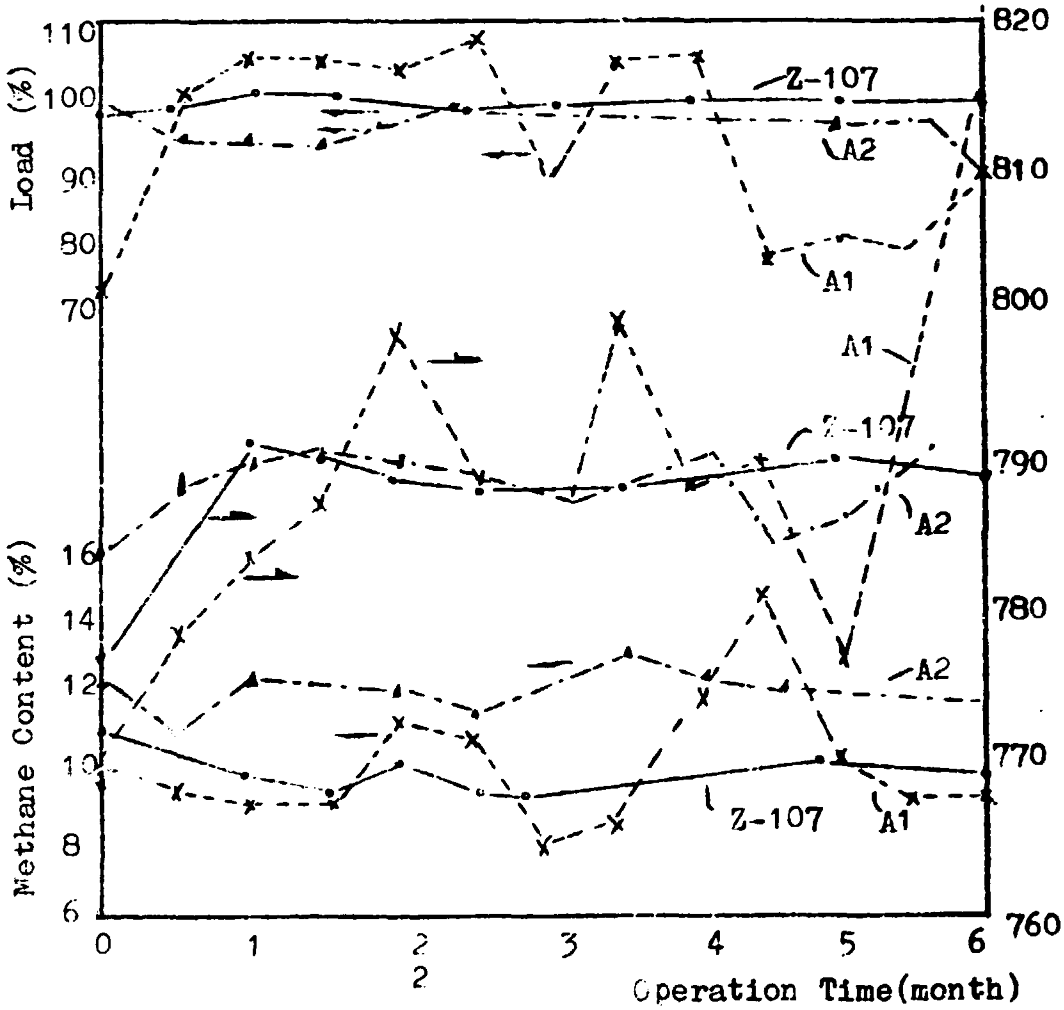

Figure 2 Performances of Catalysts Z-107, A1 and A2 Used in the Large Scale Ammonia Plant

SECONDATY REFORMING CATALYST

Normally, the mixed gas enters into the catalyst layer of the secondary reformer at about 1200 °C. But the damage of the mixer or the failure of air flow control may cause the catalyst layer locally overheated seriously, even making the catalyst sinter into cakes as happened in some ammonia plants. In order to reduce the unfavourable effect of the possible local overtemperature on the secondary reformer catalyst, in recent years a heat resistant catalyst bed has been added to the top of the secondary reformer in many large scale ammonia plants. This measure is of advantage. For this reason we developed Type Z-204 secondary reforming catalyst and Z-204R heat resistant catalyst being used together with Z-204. Their main properties are listed in Table 5.

After working on the volatile velocity and activity of nickel at high temperature and their effects on heat resistivity, we determined to develop the nickel base heat resistant catalyst of Type Z-204R.

1) Volatile velocity of Nickel at High Temperature:

It has been known that nickel volatilizes at high temperature and high vapor-hydrogen atomsphere into gas phase by forming $Ni(OH)_2$, that is:

$$Ni + 2H_2O\ (vapor) = Ni(OH)_2\ (gas) + H_2\ (gas)$$

Table 6 shows the calculation results of equilibrium volatile quantity of nickel based on the above reaction equilibrium under the operating conditions (temperature, gaseous composition and load etc.) of the secondary reformer in the large scale ammonia plant.

Table 5 Main Properties of Catalysts Z-204 & Z-204R

Catalyst	Size (mm) & Shape	Side Crush Strength (kg/gr)	Bulk Density (kg/l)	Chemical Composition (% weight)					
				Al_2O_3	CaO	NiO	SiO_2	K+Na	S Cl As P
Z-204	Ø 19x19x9 (ring)	50	1.16	69	12	18	0.2	0.2	trace
Z-204R	Ø 19x17x10 (ring)	50	1.10	90	3.5	6	0.2	0.2	trace

Since the carrier will influence the volatilization of NiO in catalyst and the residence time of the feed gas within the heat resistant catalyst layer is rather short, it is difficult to reach the volatile equilibrium of nickel in the gas phase. Moreover, owing to the reforming endotherm during the operation the gas temperature in the nickel base heat resistant catalyst will decrease some 100–140 °C. Therefore the practical volatile quantity of nickel in the use of Z-204R catalyst should be less than the data listed in Table 6. Since research reports on the nickel volatile velocity have been published scarcely we measured the practical volatile quantity of nickel in the operated catalyst Z-204R at the top of the secondary reformer of the large scale ammonia plant. The measured practical value of nickel volatilization is only 62% of the equilibrium volatile quantity. Based on this percentage the practical volatile quantity of nickel in the secondary reformer can be calculated and are listed in Table 7.

Table 6. Volatile Equilibrium Calculation Value of Nickel in the Secondary Reformer of the Large Scale Ammonia Plant

Temperatures	Average VolatileQuantity of Nickel per year (kg)	
(oC)	Top of Heat Resistant Catalyst Layer	Bottom of Heat Resistant Catalyst Layer
1000	5.95	2.95
1100	33.8	16.7
1150	70.6	34.9
1200	142.5	70.7
1300	506.8	250.8

Table 7. Practical volatile Quantity of Nickel in the Secondary Reformer of the Large Scale Ammonia plant

Temperature	Practical Volatile Percentage of Nickel in Z-204R per year (% weight)		
(°C)	Top of the Secondary Reformer	Bottom of Heat Resistant Catalyst layer	whole Z-204 Catalyst Layer
1000	0.80	0.40	10.6
1100	4.50	2.22	
1150	9.40	4.70	
1200	19.0	9.40	

Note: on the basis of 5% content of NiO in Z-204R

Table 8. Activities of Various Heat Resistant Catalysts at High Temperatures

Catalyst Designation	Active Composition	Relative Activities^{x} (%)			
		900°C	1000°C	1100°C	1200°C
Z-204^{R}	Ni	70.6	85.5	100	100
C1^{xx}	Cr	12.3	24.8	47.9	79.8
C2^{xx}	Cr	8.8	20.6	31.1	58.2

Notes: ^{x} on the basis of Z-204R heat resistant catalyst activity as 100 at 1200°C.

^{xx}C1 & C2 are the commercial catalysts on the international market.

It can be seen from Table 6 and Table 7 that the practical volatile quantity of nickel in the secondary reformer heat resistant catalyst layer is controlled by the volatile kinetics. When Z-204R resistant catalyst is used in the secondary reformer the practical volatile quantity of nickel per year is about 10%.

2) Activity at High Temperature:

The experimental results listed in Table 8 show that the activity of Z-204R at 900 °C has already reached a level of activity that the normal commercial chromium heat resistant catalyst has at 1200 °C.

The activity of Z-204R catalyst which has been used for more than one year in the secondary reformer of the large scale ammonia plant is still higher than that of chromium base heat resistant catalyst. As a result of high activity, when Z-204R nickel base heat resistant catalyst is used the reaction within the catalyst layer is more rapid and temperature falls down much more, offering Z-204R better function in protecting the reforming catalyst in bottom portion of the secondary reformer.

3) Heat Resistivity:

The heat resistivity of the agglomerating type catalyst depends mainly on its carrier. During the devolopment and the application of the catalyst in commercial units no obvious effect on the heat resistivity has been found in presence of nickel. Table 9 lists some data showing the heat resistivity. After being operated in the range of 1200 °C for more than one year in the commercial reformer the catalyst strength increased slightly and the physical-chemical parameters changed a little while C1 catalyst changed drastically. When carrying out the sudden hot or cold investigation for sustaining the violent change of temperature caused by the air addition or cut-off in the secondary reformer, Z-204R has been proved to have an excellent suitability.

Table 9. Heat Resistivity of A Few Heat Resistant Catalysts

Catalyst Designation	Relative Strength (%)	Specific Surface Area (m^2/g)	Pore Volume (ml/g)	Average Pore Radius (A^0)	No. of Sudden Hot or Cold Tests^x	Appearance
Z-204R						
(New)	100	3.36	0.217	1291	10	Without Damage
(used)	112	1.77	0.191	2158		
Cl^{xx}						
(new)	100	26.7	0.329	246	2	Edges Damaged Greatly
(used)	72	1.0	0.428	8500		

Notes: xx This denotes the number of tests that were repeatedly conducted from 1200°C to cold water without big crack.

xx Cl is a commercial heat resistant catalyst on the international market.

Additionally, there are other advantages of less toxicity and less pollution etc. in the maunfacture of nickel base heat resistant catalyst. Its manufacturing cost is similar to that of chromium base heat resistant catalyst.

In short, the research results of nickel volatile velocity, activity, strength and heat resistivity etc. show that it is feasible to use Z-204R nickel base heat resistant catalyst. This has also been proved in the practical operation of the large scale ammonia plants.

The performances of Z-204R and Z-204 used together in the secondary reformer of the large scale ammonia plants shown in Table 10.

Table 10 Performances of two Catalysts in the Same Large Scale Ammonia Plant[x]

Catalyst	Load (%)	Outlet Pre. kg/cm^2	Pre. Drop kg/cm^2	Inlet Temp. °C	Outlet Temp. °C	CH_4 in Inlet gas %	CH_4 in Exit gas %	Temp. Approach to Equilibrium °C
Design Figure	100	30	0.6	822	1003	9.60	0.33	15-41
Z-204R Z-204	100	30	0.5	805	948	10.15	0.35	-9
C+D[xx]	100	30	0.5	805	967	9.97	0.31	-6

Notes: [x] Results of two catalysts taken after a half year operation

[xx] C & D are the commercial catalysts on the international market.

The data in Table 10 show that when using Z-204R and Z-204 catalysts there is a normal temperature distribution, normal pressure drop in the reformer, making the reformed gas composition meet the requirement of design. This set of catalysts promotes the reaction to attain equilibrium basically, which demonstrates the catalyst activity is excellent. The performances of Z-204 and other catalyst after two years operation are listed in Table 11.

Table 11 Performances of Z-204 and Cther Catalyst after Two Years Operation

Catalyst DDesignation	Side Crush Strength kg/gr	Relative Activity %	Specific Surface Area m^2/g	Pore Volume ml/g	Porosity %	Average Pore Radius ^{o}A
Z-204 (new)	50	100	50	0.197	47	78
(used)	45	60	7.7	0.289	56	750
x D (new)	45-50	100	17.1	0.2371	42	277
(used)	10	40	1.0	0.3265	54.9	8000

Data of Table 11 show that Z-204 catalyst still has sufficient activity after two years operation and the stability of its activity and structure is better than that of the same kind of commercial catalyst D.

Since a close attention was paid to the harmful impurities during manufacture, it has never happened in the use that the performance of the waste heat boiler is influenced by the silicon migration.

It can be seen from the aboce description that adoption of Z-204R heat resistant catalyst together with z-204 reforming catalyst may successfully satisfy the needs of the secondary reformers in the large and middle scale ammonia plants.

PROSPECT

Normal operation of the large scale ammonia plant is unseparable from having good quality catalyst. Any improvement in the reforming catalyst always promotes further development of ammonia plant.

It is well known that the steam methane reforming reaction velocityis controlled by the internal diffusion under commercial conditions.(7)

A lot of research results show that the reforming reaction is essentially conducting on the outside surface of catalyst particles. (8,9) Using the shorter ring catalyst of Ø 16x8x6 mm on the top of the tubes in the large scale ammonia plants has gained distinct effects. But further decrease of the particle size may lead to a quick increase of the resistance inside the tubes. This not only hinders the catalyst in its normal operation, but lowers its economics. (10)

Our research work suggests that one of the ways of solving the above problems is to adopt a new and reasonable appearance of the catalyst. A fine appearance will not only provide a larger surface area, but also allow the catalyst to have less resistance and possess a high strength.

On the other hand, the performances of some ammonia plants in recent years indicate time and again that the strength of agglomerating type catalyst is adequate.(11) Moreover, the enduring stability of their activity should be raised and its anti-carbon deposit property should be improved also. Our work shows that when some promoters are added into the reforming catalyst its anti-carbon deposit property and activity stability will be improved to a certain degree.

After choosing a new appearance and adding certain promoters, it is possible to develop a new type catalyst with high apparent activity, high strength, less resistance and allowable to be operated at a lower water/ carbon ratio. Thanks to this catalyst the reforming process may probably take on an entirely new aspect.

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