METHOD FOR REACTIVATION OF A CATALYST USED IN STEAM REFORMING OF HYDROCARBONS

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1. Introduction

Osaka Gas Company,Ltd. has been bringing in LNG, a clean fuel, from overseas since late 1972. With the necessity of the fact that our company smoothly converts its system from manufactured gas to natural gas distribution,the establishment of SNG(Substitute Natural Gas) production technology is essential if any possibility of a short supply of LNG is taken into account.

We have already developed the MRG(Methane Rich Gas) process, a low temperature steam reforming process, jointly with Japan Gasoline Company(JGC). Although this process, a SNG process using LPG or Naphtha with a nickel type reforming catalyst, is of good efficiency, it is considered that a SNG process with a better reforming catalyst can be expected to be of higher efficiency. As the result of extensive investigation, we have recently succeeded in developing a new steam reforming catalyst completely different from conventional catalysts. This catalyst,SN-108, has many excellent characteristics as compared with conventional steam reforming catalysts. In particular, it is a great advantage that this catalyst can be reactivated perfectly by the newly developed method.

It is our intention to explain pricipally about the characteristics of SN-108 and the method for reactivation.

2. Catalyst

The conventional catalysts used in low temperature steam reforming of hydrocarbons are usually nickel type.
On the other hand, SN-108 has a γ-Alumina oxide core impregnated with active metal which is not nickel.
The characteristics of SN-108 are as follows.

(1) High activity and long life.
(2) Resistance to the deposition of carbonaceous materials.
(3) Operable in the low temperature range and with a low steam to carbon ratio,such as 1.5 and 0.7 respectively at 1st and 2nd stage of two stages reactors.
(4) Handling is simple and no hydrogen reduction is reguired.

In addition to these characteristics,SN-108 can be completely reactivated by the specified method which we have recently developed. Furthermore, it has been found that SN-108 has a good performance in gasifying heavier distilates such as kerosene,gas oil,V.G.O. etc.

SN-108 has already been used for three winter seasons in a commercial plant of a daily output of 200,000 Nm^3/day to reform straight run naphtha having an end point 180°C (Test Naphtha) and also subjecting to reactivation during this period.
In these operations,the characteristics of SN-108 has been comfirmed. Fig.1 shows the catalyst deterioration with passing of time in the third operation. The reaction conditions are as follows.

steam / carbon ratio : 1.5
reaction pressure and temperature : 12 Kg/cm^2 G, 490°C

3. Reactivation

3.1 Method of reactivation

Typical conventional procedures for reactivation are treatments with hydrogen,steam or oxigen,which are mainly effective for the elimination of carbonaceous materials deposited on the catalysts. Our new reactivation system consists of two stages of chemical treatment essentially different from conventional ones. It is particularily noted that the combination of two chemical treatments is essential for the parformance of reactivation.
The system cycle may be repeated depending on the extent of catalytic activity deterioration. Even if the catalytic activity deteriorates completely after being used, it is recovered to the state of flesh catalyst by 6 to 8 treatments.

Fig.2 shows the general process flow.

3.2 Effect of reactivation

1. Sample

The sample to be reactivated is the catalyst which had been used in a commercial plant for 4300 hours to reform Test Naphtha with steam and whose activity deteriorated completely.

2. Catalytic activity

Fig.3 shows the temperature profiles of steam reforming reaction using Test Naphtha. It can be found that the catalytic activity is recovered depending on the number of treatment.

3. Catalytic properties

Table 1 shows the typical catalytic properties of fresh catalyst,used catalyst and reactivated catalyst.

Table 1. Typical property of tha catalyst

	sample / property	fresh cat.	used cat.	reactivated cat.
catalyst	carbon content (wt%)	0.2	6.0	3.0
	sulfur content (wt%)	0.00	0.09	0.00
	relative active metal content	1	1	1
carrier	crush strength (kg)	20	7.3	7.0
	surface area (m^2/g)	140	90	95
	pore volume (cc/g)	0.46	0.38	0.38

4. Chemical state of active metal

Fig.4 shows XPS spectra of the three kinds of catalysts. It became clear that the active metal consists of three kinds of chemical state,the relative ratios of three states change after being used and the chemical state of used catalyst is recovered to the almost same state of fresh catalyst by reactivation.

3.3 Mechanism of reactivation

In general,catalytic steam reforming reactions of hydrocarbons result in deposition of various materials such as carbonaceous and sulfurous materials on the catalyst. In addition,these reactions often result in a sintering of active metal particles causing their mutual cohesion,whereby the size of active metal particles enlarged and the dispersibility consequently lowered. Further,the physical or chemical constitution and behaviour of active metal may be gradually changed during the catalytic reactions. From the results in Table 1,it became clear that carbonaceous and sulfurous materials on the catalyst were eliminated by reactivation. Especially sulfurous materials was removed completely. Moreover,the observations by transparent electron-microscope gave the fact that there existed some sintered active metal particles on the catalyst after being used which disappeared after reactivation. Furthermore,as indicated in Fig.4,active metal of used catalyst was recovered to the chemical state of active metal of fresh catalyst. Consequently it may be concluded from these facts that our reactivation method is effective for the reduction or elimination of all of these adverse factors.

It may be noted,as stated in section 3.1,that conventional reactivation treatment with hydrogen,steam or oxigen is effective for the removal of carbonaceous material deposited on the catalysts,but not for the elimination of sulfurous materials and the recovery of chemical constitution of active metal. We have already found that conventional reactivation method has completely no effect on the recovery of the catalytic activity of SN-108 and furthermore our reactivation method is not effective for the recovery of the activity of conventional nickel type catalysts.

4.Summary and Conclusions

We have developed the new catalyst,SN-108,for low temperature steam reforming of hydrocarbons which has various excellent characteristics as compared with conventional nickel type catalysts. In particular,SN-108 is operable with a extremely low steam to carbon ratio,which enables SNG process with the catalyst to be of much higher efficiency. Furthermore,we have developed the new reactivation method for SN-108 essentially different from conventional methods and succeeded in commercializing this method. We believe that the process with SN-108 can make the great many of advantages in the field of steam reforming of hydrocarbons.

In Japan where stringent environmental protection regulations are being enforced,there has been a trend of using lighter fuel oil and it is considered inevitable that there will be greater surplus hereafter of residual oil. With this background,we will continue to investigate the catalytic activity and the reactivation method for SN-108 with residual oil.

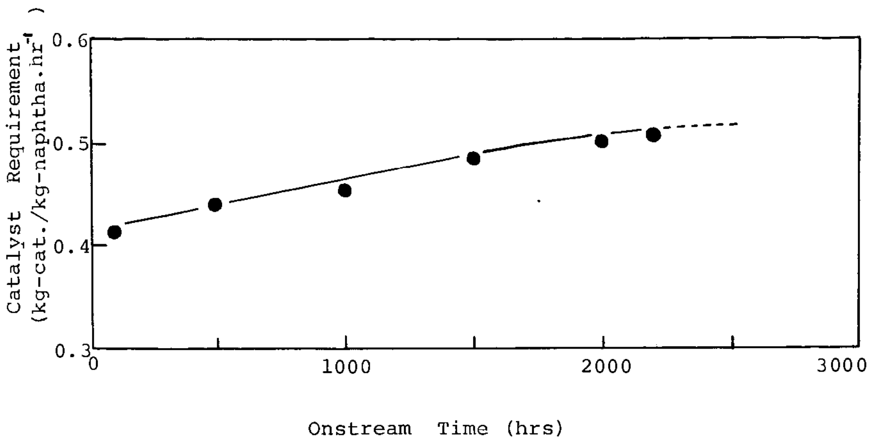

Fig.1 Activity deterioration curve of SN-108

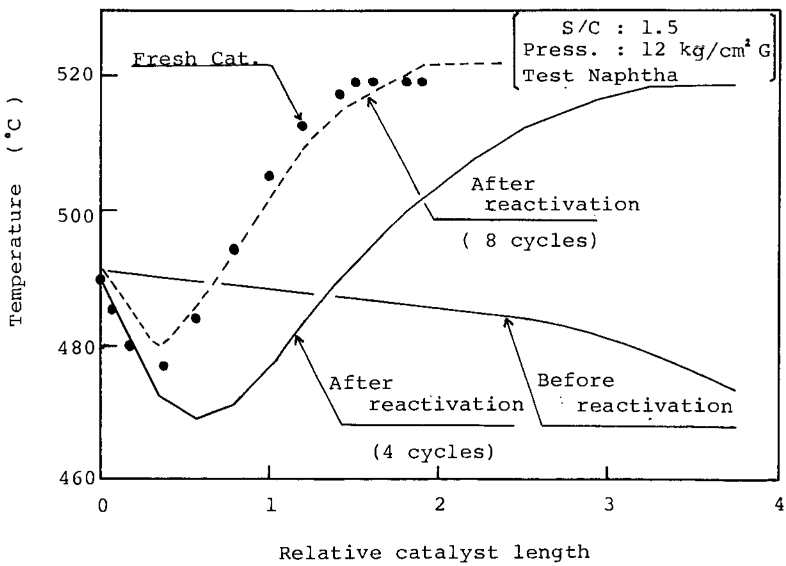

Fig.2 Recovery of the catalytic activity

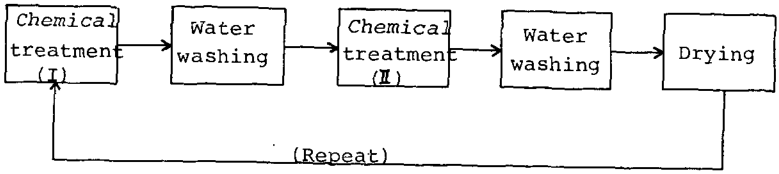

Fig.3 General process of reactivation

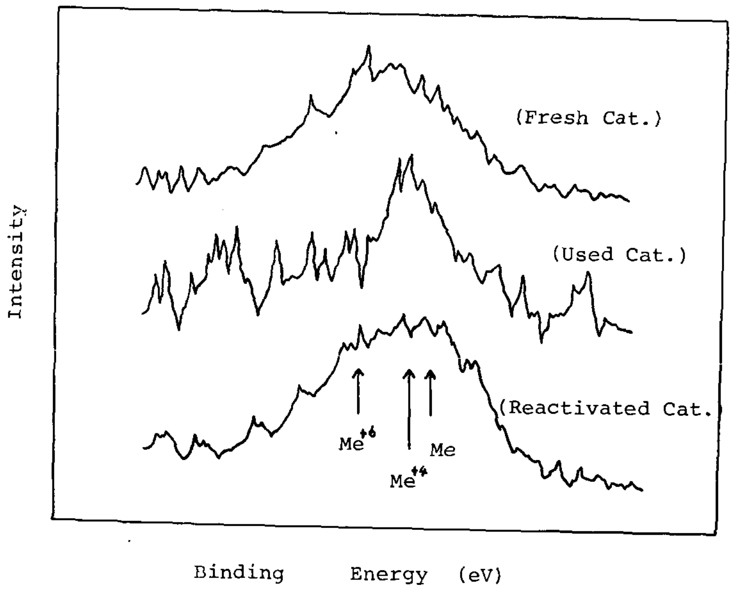

Fig.4 XPS spectra of active metal