

## THERMAL ANALYSIS OF SPENT STEAM-REFORMING CATALYSTS

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### ABSTRACT

Thermal analysis is a group of techniques in which changes in characteristic properties, of a physical or chemical nature within a substance, are measured as a function of temperature. In catalyst studies, thermal analysis may be used to obtain information on the thermal stability, composition, deactivation, activity and life of a catalyst. The method is especially useful for studying the transformations that occur in or on a catalyst when heated. These transformations include decomposition, phase transition, adsorption, absorption, desorption, dehydration, degradation and solid-state and gas–solid reactions.

In this paper, the thermal analysis (TG and DTA) results of spent steam-reforming catalysts are presented. Ni/Al<sub>2</sub>O<sub>3</sub> catalysts, which had been in operation in a steam reformer for about 18 months, gave exothermic effects with corresponding weight gain in the temperature range 20–1130 °C. Ni/CaO/Al<sub>2</sub>O<sub>3</sub> catalysts, which had been in use for 30 months, however, gave endothermic and exothermic effects with weight loss between 20–850 °C, and an exothermic effect with weight gain at about 900 °C. These results and the significant changes observed in the properties of the catalyst along the reformer tube are discussed.

### INTRODUCTION

The catalytic steam reforming of methane is used in the manufacture of synthesis gases for ammonia, methanol and hydrogen production. The process is being used in petrochemical plants and refineries within Saudi Arabia. Commercial catalysts for this process have nickel as the active ingredient. The nickel is supported by an alumina carrier and is promoted with oxides of calcium, magnesium, aluminum or titanium and their mixtures. The nickel content varies from 10–25% according to operating conditions and type of process [1].

The nickel component of the catalyst is generally in the oxidized form (NiO) in the fresh catalyst and is reduced to the active metal (Ni) in the industrial reactors. Thus, the active nickel content can be used to explain ageing and deactivation processes. The literature, however, does not have much data on the behaviour of commercial catalysts in industrial reactors.

TABLE 1

Phenomena studied by TG and DTA and effects observed during the heating cycle [4]

Phenomenum	Change in weight		Thermal effect (DTA)	
	Gain	Loss	Endothermic	Exothermic
Adsorption and absorption	1	–	–	–
Desorption	–	1	1	–
Dehydration or desolvation	–	1	1	–
Crystalline transition	–	–	1	1
Melting	–	–	1	–
Vaporization	–	1	1	–
Sublimation	–	1	1	–
Decomposition	–	1	1	1
Oxidative degradation	–	1	–	1
Solid-state reaction	–	1/2 <sup>a</sup>	1	1
Solid–gas reaction	1	–	1	1

<sup>a</sup> Some solid-state reactions proceed with weight loss e.g.  $A(s) + B(s) \rightarrow C(s) + D(g)$  but others show no weight change e.g.  $A(s) + B(s) \rightarrow C(s) + D(s)$  or  $A(s) + B(s) \rightarrow AB(s)$ .

Thermal analysis techniques may be applied to the study of the behaviour of commercial catalysts used in industrial reactors [2,3]. Differential thermal analysis (DTA) is a means of measuring the amount of heat evolved or absorbed and the temperature at which these changes take place within the material. Thermogravimetry (TG) is a technique in which the change in mass of a substance is measured as a function of temperature. Thus, by combining the results of TG and DTA, it is possible to deduce and establish, as illustrated in Table 1, the transformation phenomena that occur when a catalyst is heated [4]. These techniques (TG and DTA) can be used either qualitatively, as finger-printing techniques to identify processes, or quantitatively.

In this study, thermal analysis techniques (TG and DTA) were used to study the thermal decomposition, nickel oxidation and other thermal changes that occur within commercial steam-reforming catalysts as a function of position within the reactor.

## EXPERIMENTAL

Two types of spent reforming catalysts were studied. The first type, Ni/Al<sub>2</sub>O<sub>3</sub> (A) was taken after 18 months of operation in an industrial reformer, while the second type Ni/CaO/Al<sub>2</sub>O<sub>3</sub> (B) was taken after 30 months of catalyst use. The samples of the two types of catalysts were taken from different positions in the reformer tube ranging from the top to the bottom. The Ni/Al<sub>2</sub>O<sub>3</sub> catalyst samples were taken from two different levels from the top of the reactor. The sample closer to the top of the reactor was

labelled A-Top and the sample further from the top was labelled A-Bottom. The exact locations of the samples from the top of the reactor were not known. The inlet and outlet temperatures of the reactor were 480 and 790 °C respectively. The steam to carbon ratio was 3.9 and the operating pressure was 30 bar.

In the case of Ni/CaO/Al<sub>2</sub>O<sub>3</sub> catalysts, the samples were taken at 1, 5, 8 and 11 m from the top of the reactor which had inlet and outlet temperatures of about 500 and 840 °C respectively. The steam to carbon ratio was 3.2 and the operating pressure was 15 bar.

All samples were studied on a Netzsch simultaneous thermal analyser, STA 429, from ambient temperature up to 1000 °C at a heating rate of 10 °C min<sup>-1</sup> in a dynamic air atmosphere (150 ml min<sup>-1</sup>) with alumina as a reference material. 150 mg of catalyst sample was ground and placed in one alumina crucible. The same weight of aluminum oxide (Al<sub>2</sub>O<sub>3</sub>), which undergoes no thermal change in the temperature range of the experiment, was placed in an identical crucible as a reference sample. The temperature of the sample was measured by thermocouples of platinum and of platinum plus 10% rhodium. The parameters recorded simultaneously were temperature (*T*), change in weight (TG) and difference in temperature between sample and reference (DTA). In the thermograms, the weight loss, the differential temperature and the temperature of the samples are plotted simultaneously. The endothermic peaks are shown downwards and the exothermic peaks are shown upwards with respect to the base line.

## RESULTS AND DISCUSSION

The working conditions (temperature, pressure, concentration and flow rate) are not the same throughout the whole length of the reactor reformer tubes. For example, the working temperature increases from the top to the bottom of the tube and also local overheating is possible. These sources of variation together with the reoxidation procedure followed after shutdown of a commercial reformer may account for some differences in the results obtained.

Commercially, the reformer tubes are fixed-bed, down-flow reactors packed with an appropriate reformer catalyst, and are about 12 m long.

### *Ni / Al<sub>2</sub>O<sub>3</sub> catalysts*

The fresh Ni/Al<sub>2</sub>O<sub>3</sub> catalyst, which contained about 12% Ni, did not undergo any thermal or weight changes in the temperature range of testing (Table 2). This indicates that the fresh sample did not contain significant amounts of volatiles or oxidisable material. Thus, the nickel as expected was mainly in the oxidised form. It also indicates that the active component, the

TABLE 2

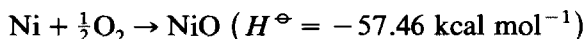
Thermal analysis results of Ni/Al<sub>2</sub>O<sub>3</sub> catalyst samples

Sample	Temperature range (°C)	Thermal effect <sup>a</sup>	T <sub>max</sub> of DTA peak (°C)	Wt. change (%)	Total wt. change (%)
Fresh	20–1000	–	–	0.0	0.0
Spent A-top	20– 750	Exo	460	0.2	0.8
	750–1000	Exo	880	0.6	
A-bottom	20– 750	Exo	480	0.3	1.8
	750–1000	Exo	780	1.5	

<sup>a</sup> Thermal effect: exothermic or endothermic.

promoters (as oxides) and the support do not undergo any chemical or phase changes in the temperature range 20–1000°C.

Differential thermal analysis (DTA) of the spent samples (Fig. 1 and Table 2) showed two exothermic peaks with corresponding weight gains in the temperature range 300–900°C. This is an indication (Table 1) of a solid–gas reaction (i.e. oxidation of nickel). Oxidation of metallic nickel is exothermic according to the reaction



The metallic nickel content of the spent catalyst may be calculated assuming

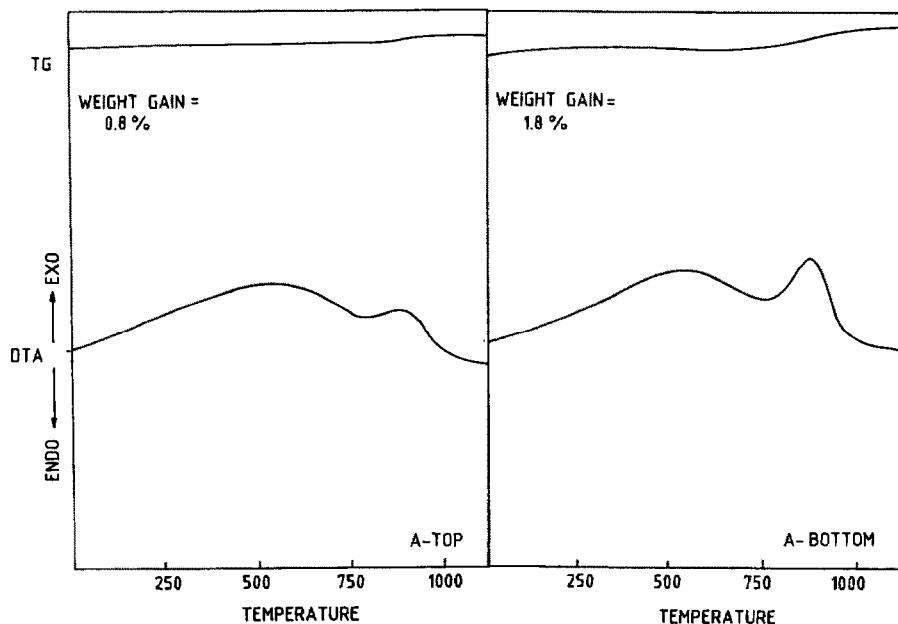


Fig. 1. Thermal analysis of spent Ni/Al<sub>2</sub>O<sub>3</sub> catalysts.

the weight gain is due to the oxidation of metallic nickel to nickel oxide (NiO). A comparison between the fresh and spent thermal analysis results clearly indicates that the major difference in thermal behaviour is due to the presence of metallic nickel (the active component). The metallic nickel is believed to be within the catalyst whereas the nickel on the surface is in the oxidised form. This accounts for the difference between the nickel content of the fresh sample and the metallic nickel content of the spent sample. TG analysis permits the determination of metallic nickel alone and not nickel in the form of either nickel aluminate or nickel oxide [5].

The total Ni content in catalysts is generally determined after a complete dissolution of the sample (in acids or by alkaline fusion) by gravimetric, calorimetric or polarographic methods [6]. TG analysis showed that the increase in sample weight due to nickel oxidation was 0.8 and 1.8 for the top and bottom samples which corresponds to a metallic nickel content of 2.93 and 6.6% respectively. This indicates a significant amount of nickel in the spent catalyst in the form of NiO, due to reoxidation of nickel on the surface and/or of nickel aluminate resulting from catalyst-support interaction.

Thermal analysis results indicated that the catalyst samples showed similar thermal behaviour regardless of their position in the reformer tube: two exothermic peaks with corresponding weight gains in the temperature range 20–1000 °C. The concentration of metallic nickel tended to increase from the top of the reformer tube to the bottom. In a similar study [5] it was found that the metallic nickel content increased from the top of the reactor to the bottom in a manner similar to the trend observed in this study. The observed trend may be due to the fact that the top environment is more oxidising (i.e. less reducing) than the bottom. Due to the reforming reaction, the gas stream becomes more reducing as it moves down through the reactor bed.

#### *Ni / CaO / Al<sub>2</sub>O<sub>3</sub> catalysts*

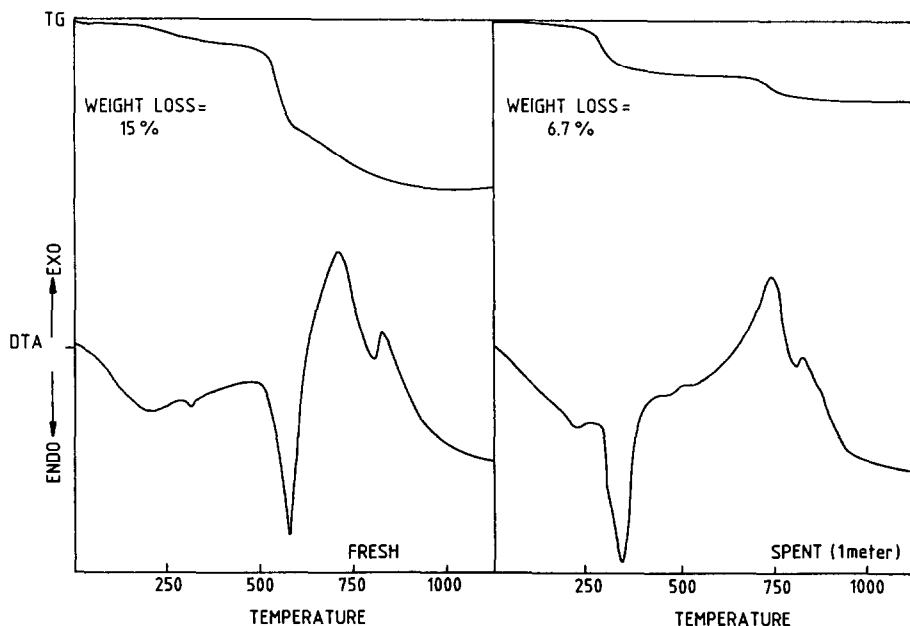
The other type of commercial steam reforming catalyst studied was Ni/CaO/Al<sub>2</sub>O<sub>3</sub> (Ni = 15%, CaO = 7% and Al<sub>2</sub>O<sub>3</sub> = 78%). Samples were taken from four different positions in the reformer tube: 1, 5, 8 and 11 m from the top of the reactor. The samples had been in use for 30 months. A fresh sample of the same catalyst was subjected to thermal analysis under the same testing conditions. Thermal analysis results are presented in Table 3 and Figs. 1–5.

The fresh sample (Fig. 1) showed endothermic effects in the temperature range 20–600 °C and two exothermic effects in the temperature range 600–1000 °C. The weight losses corresponding to the endothermic and exothermic effects were 8.3 and 6.7% respectively. The endothermic peak at 125 °C is ascribed to loss of moisture. The endothermic peaks at 270 and 560 °C with corresponding total weight loss of about 6.0% are due to the

TABLE 3

Thermal analysis of spent catalyst samples Ni/CaO/Al<sub>2</sub>O<sub>3</sub>

Sample	Temperature range (°C)	Thermal effect <sup>a</sup>	T <sub>max</sub> of DTA peak (°C)	Wt. change (%)	Total wt. change (%)
Fresh	20– 750	Endo	125	– 2.3	– 15.0
	270– 400	Endo	270	– 0.3	
	400– 600	Endo	560	– 5.7	
	600– 800	Exo	700	– 5.4	
	800– 1000	Exo	830	– 1.3	
Spent 1 m	20– 230	Endo	175	– 0.5	– 6.7
	230– 420	Endo	315	– 4.0	
	420– 500	Endo	465	– 0.7	
	500– 800	Exo	720	– 0.9	
	800– 1000	Exo	800	– 0.6	
5 m	20– 415	Endo	325	– 8.5	– 9.1
	415– 760	Endo	480	– 1.0	
	760– 1000	Exo	900	+ 0.4	
8 m	20– 415	Endo	315	– 8.3	– 9.8
	415– 760	Endo	462	– 1.6	
	760– 1000	Exo	900	+ 0.1	
11 m	20– 420	Endo	320	– 8.8	– 10.0
	420– 750	Endo	460	– 1.3	
	750– 1000	Exo	900	+ 0.1	

<sup>a</sup> Thermal effect: Exo = exothermic, endo = endothermic.Fig. 2. Thermal analysis of fresh and spent Ni/CaO/Al<sub>2</sub>O<sub>3</sub> catalysts.

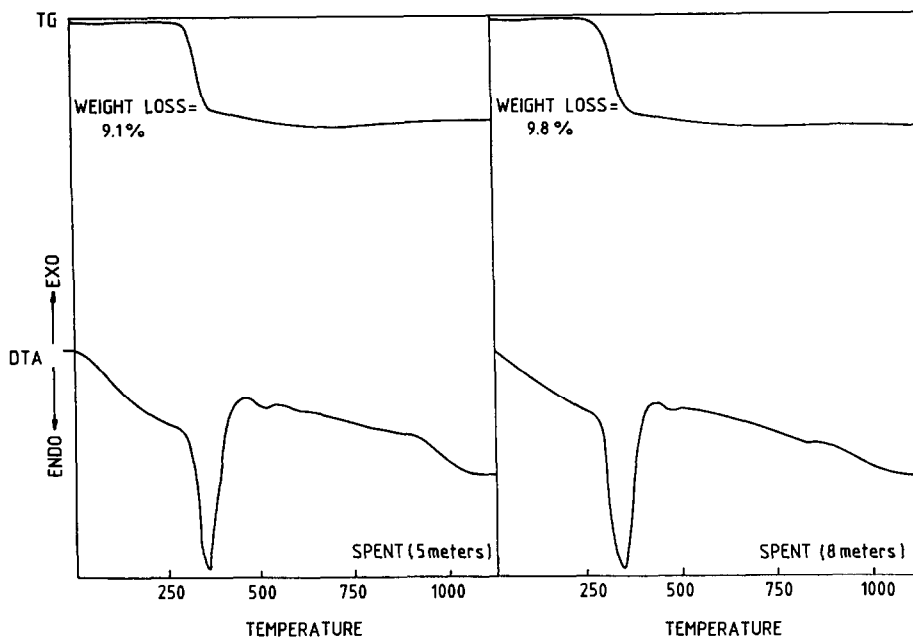


Fig. 3. Thermal analysis of spent Ni/CaO/Al<sub>2</sub>O<sub>3</sub> catalysts taken from 5 and 8 m from the top of the reformer tube.

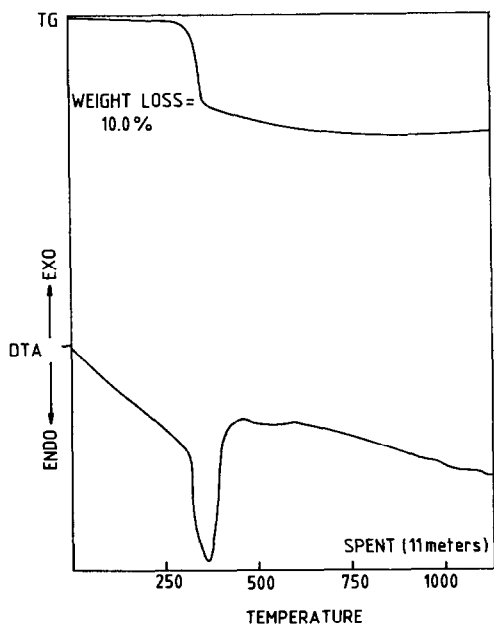


Fig. 4. Thermal analysis of Ni/CaO/Al<sub>2</sub>O<sub>3</sub> catalyst taken from 11 m from the top of the reformer tube.

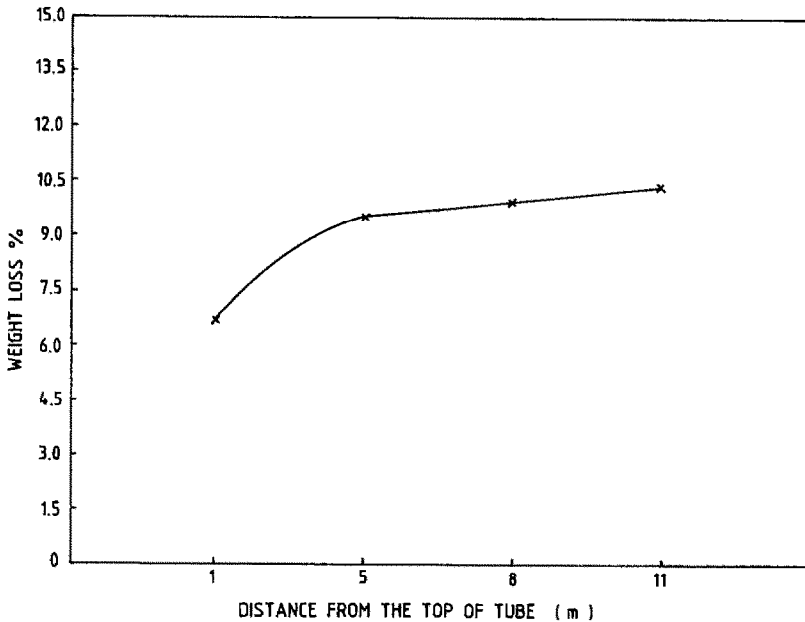


Fig. 5. Weight loss of spent Ni/CaO/Al<sub>2</sub>O<sub>3</sub> catalysts taken from different locations in the reformer tube.

decomposition and removal of chemically bound volatiles or to a solid-state reaction. The exothermic peaks at 700 and 830 °C with corresponding weight loss of about 6.7% are due to decomposition, dehydroxylation of alumina and/or a solid-state reaction accompanied by phase transition.

The thermal behaviour of the sample taken 1 m from the top of the reformer tube was similar to that of the fresh sample. The DTA curve revealed three endothermic effects in the range 20–600 °C. All thermal effects were associated with weight loss (6.7%). Beyond the first 1 m from the top, the remaining spent samples showed similar thermal behaviour: two endothermic effects in the range 20–500 °C and an exothermic peak in the range 500–1000 °C. The endothermic effects are associated with weight loss, while the exothermic effect appears to be associated with a small weight gain. The total weight loss of the four samples increased with depth in the reactor as shown in Fig. 5.

The endothermic effects up to 400 °C in both fresh and spent samples are due to the loss of loosely and rigidly bound water. The endothermic change between 400 and 600 °C is believed to be the net result of exothermic carbon combustion and endothermic decomposition (of carbonates). The exothermic effects between 600 and 1000 °C are the net result of nickel oxidation, oxidative degradation and a solid-state reaction. At about 900 °C, metallic nickel oxidation appears to be the dominant thermal effect.

The amount of metallic nickel present in the spent samples as determined by the net weight gain in the TG analysis is too small to draw any



conclusions on the trend in the tube. However, it appears that at more than 5 m from the top of the tube, the metallic nickel decreases marginally with depth. The small net weight gain in TG may be due to the oxidation of metallic nickel to nickel oxide during the shutdown and subsequent storage periods. It may also be due to the conversion of metallic nickel to stable products of catalyst–support interaction.

The increase in weight loss with depth in the reactor appears to be mainly due to the increase of loosely and rigidly bound water. Also the combined effect of carbon combustion and decomposition (e.g. of carbonates) at about 460 °C appears to increase with depth in the reactor. This also partly accounts for the increase in weight loss with bed depth.

## CONCLUSIONS

Differential thermal analysis and thermogravimetric analysis can be used as rapid methods to follow the changes in the active nickel component, as well as other transformations that occur within supported nickel catalysts, as a function of position in industrial reactors. Spent Ni/Al<sub>2</sub>O<sub>3</sub> catalysts gave exothermic peaks with corresponding net weight gain indicative of oxidation of metallic nickel. The metallic nickel content increased from the top to the bottom of the reformer tube. Ni/CaO/Al<sub>2</sub>O<sub>3</sub> catalysts showed significant thermal changes with net weight losses which increased with distance from the top of the reactor. The thermal changes were associated with dehydration, decomposition (of carbonates) and solid–gas reactions (mainly carbon combustion and nickel oxidation). The reoxidation of metallic nickel during shutdown and the conversion of active metal catalysts to products of catalyst–support interaction affect the reliability of determining metallic nickel content using thermal analysis technique.

## ACKNOWLEDGEMENT

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