Thermochimica Acta, 185 (1991) 73–82
Elsevier Science Publishers B.V., Amsterdam

The measurement of the extent of reduction of steam-re-forming catalysts using thermal analysis techniques

Yaw D. Yeboah, Ali G. Maadhah and Abdullah M. Aitani

The Research Institute, King Fahd University of Petroleum and Minerals, Dhahran 31261 (Saudi Arabia)

(Received 20 November 1990)

Abstract

The thermal decomposition, the nickel oxidation and other thermal changes in commercial NiO/Al_2O_3 catalysts were studied over the temperature range 20–1000°C. The thermal analysis (TG and DTA) results of the reduced steam-re-forming catalysts were used to determine the extent of reduction of the catalyst to the active metal (nickel). The metallic nickel content in the reduced catalyst samples determined by the rapid thermal technique compared fairly quite well with results obtained by the longer chemical analysis method. The thermal analysis of the reduced steam-re-forming catalysts each showed, regardless of reduction conditions, one exothermic peak with a corresponding gain in weight in the temperature range 20–1000°C.

INTRODUCTION

Thermal analysis techniques such as differential thermal analysis (DTA) and thermogravimetry (TG), are used in catalytic investigations as a tool for the characterisation of the catalysts. These techniques are especially useful for studying the transformations that occur in or on a catalyst when heated. Thermal analysis employed in the determination of the extent of reduction of supported nickel catalysts involves the measurement of weight gain and heat evolved during the oxidation of the metal. Supported nickel catalysts are widely used in many industrial applications, including hydrogenation, hydrotreating, steam re-forming and methanation reactions. These reactions are used widely in the refining and petrochemical industries for the manufacture of hydrogen, methanol and ammonia. The nickel component of the catalyst is generally in the oxidised form (NiO) in the fresh catalyst and is reduced to the active metal (Ni) in the industrial reactors. Thus, the active nickel content in the steam-re-forming catalyst can be used to explain the activity behaviour of commercial catalysts in industrial reactors. In most cases the catalyst activation involves reduction by a suitable gaseous reducing agent [1–4]. The proportion of metallic nickel in reduced catalyst

0040-6031/91/$03.50

samples is an important parameter used to estimate the extent of reduction. If both the metallic nickel and the total nickel content of the catalyst are known, the percent reduction can be calculated.

The extent of reduction can be determined by chemical or thermal analysis techniques. The chemical analysis method is tedious and time-consuming and involves the dissolution of the catalyst sample in dilute acid (HCl) and the subsequent determination of the metal by atomic absorption spectrometry, visible-range spectrometry or using a chelation method. In the literature, metallic nickel has been determined by selective dissolution in bromine–methanol mixture [5–7], carbonylation (formation of nickel carbonyl) [8,9] and oxygen titration [10].

Of the three most common methods of thermal analysis, thermogravimetry (TG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC), TG is the simplest, most direct and rapid technique for reduced catalyst oxidation [11–14]. The extent of reduction can be determined quantitatively by the gain in weight due to the metallic nickel oxidation [11]. The interpretation of thermal analysis curves for metallic nickel oxidation is sometimes complicated by the physical and chemical nature of the support. However, in the case of Ni/Al_2O_3 catalyst, the support is inert alumina and it is assumed that there is no interaction between the active metal (nickel) and the support over the ranges of reduction conditions. This assumption may be verified by X-ray diffraction (XRD) measurements.

In this study, thermal analysis techniques (TG and DTA) and chemical analysis methods were used to determine the metallic content of commercial steam-re-forming catalysts and, hence, the extent of reduction.

EXPERIMENTAL

Two types of commercial steam-re-forming catalysts were studied. The chemical compositions of the catalysts are presented in Table 1. The reduction experiments were performed using a modified Micromeritics Pulse Chemisorb 2700. About 3 g of the catalyst was used in each reduction experiment. Hydrogen was used as the reducing gas at different space

TABLE 1

Chemical analyses of the fresh commercial steam-re-forming catalysts studied [a]

Catalyst type	Composition (%)						
	Ni	Al_2O_3	CaO	MgO	SiO_2	Na	K_2O
A	20.3	73.6	0.06	0.05	0.06	0.11	0.16
B	12.8	83.5	0.08	0.05	0.05	0.09	0.11

[a] TiO_2, C, S and Cl were each < 0.03 wt.% in both A and B.

TABLE 2

Experimental conditions of the catalyst reduction experiments

Run	Ni loading (wt.%)	Temp. (°C)	Reducing gas	Reduction time (h)	Heating rate (°C min^{-1})	Space velocity (h^{-1})
1	20.0	400	H_2+N_2	6	15	1800
2	20.0	500	H_2+N_2	6	5	900
3	12.4	400	H_2	6	5	1800
4	12.4	500	H_2	6	15	900
5	12.4	400	H_2+N_2	16	15	900
6	12.4	500	H_2+N_2	16	5	1800
7	20.0	400	H_2	16	5	900
8	20.0	500	H_2	16	15	1800
9	20.0	500	H_2+He	16	15	900
10	20.0	400	H_2+He	16	5	1800
11	20.0	500	H_2	6	5	1800
12	20.0	400	H_2	6	15	900
13	12.4	500	H_2+He	6	15	1800
14	12.4	400	H_2+He	6	5	900
15	20.0	300	H_2+He	3	20	3600
16	20.0	600	H_2+He	3	3	450
17	20.0	600	H_2	3	3	3600
18	12.4	600	H_2	3	20	450
19	12.4	600	H_2+He	10	3	3600
20	20.0	300	H_2	10	3	450
21	20.0	600	H_2	10	20	3600
22	12.4	600	H_2	10	3	450
23	12.4	300	H_2	10	20	3600
24	20.0	600	H_2+He	10	20	450
25	20.0	300	H_2+He	10	3	3600
26	20.0	600	H_2	3	3	3600
27	20.0	300	H_2	3	20	450
28	12.4	600	H_2+He	3	20	3600

velocities. The sample was held at selected reduction temperatures for a duration of 3–16 h. At the end of the reduction experiment, nitrogen was allowed to flow through the sample until the temperature dropped to room temperature. Table 2 shows the explicit experimental conditions used for the reduction of the catalyst samples.

The DTA and TG of the fresh and reduced catalyst samples were measured using a Netzsch simultaneous thermal analyser (STA 429) from ambient temperature up to 1000°C at a heating rate of 10°C min^{-1} in dynamic air atmosphere. A detailed experimental procedure was reported earlier [15].

The chemical analysis of the fresh catalyst sample was determined using an inductively coupled plasma (ICP) spectrophotometer, Applied Research

Laboratories (ARL-3580), equipped with various channels that allow the simultaneous determination of 48 elements. The metallic nickel in the reduced catalyst samples was determined by selective dissolution in bromine–methanol mixture. The bromine and methanol were of 99.99% purity [17,18]. The total nickel (acid-soluble Ni and NiO) was determined after dissolving the sample in hot 1 : 1 aqueous HCl, using spectrophotometry. The difference between the total acid-soluble nickel and the metallic nickel results gave the amount of nickel oxide.

RESULTS AND DISCUSSION

In order to verify the chemical analysis procedure and the applicability of the thermal analysis techniques in the determination of the extent of catalyst reduction, some tests were conducted on known $Ni/NiO/Al_2O_3$ mixture samples. Four synthetic compositions were prepared by mixing metallic nickel (Ni), nickel oxide (NiO) and alumina (Al_2O_3). The metallic nickel was determined using the chemical and thermal analysis methods. The results of these tests are presented in Table 3. The results indicate a close agreement between the two methods. The recovery of metallic nickel reached 100 ± 2.0% which is within the error in reproducibility of the two methods.

The thermal behaviour of the fresh steam-re-forming catalysts did not show any significant weight or physical changes in the temperature range 20–1000°C, as shown in the thermograms of Figs. 1 and 2. This indicates that the commercial catalyst is thermally stable and confirms that the active component in the sample, nickel, is present in the oxidised form.

The thermal analysis results of reduced catalyst samples are presented in Table 4. Typical thermograms of the two types of reduced steam-re-forming catalysts studied are shown in Figs. 3 and 4.

For nickel determinations by the thermal analysis method, the oxidation of nickel by free oxygen is of special importance and proceeds according to

TABLE 3

Verification of the thermal and chemical analytical procedures for the determination of metallic nickel in $Ni/NiO/Al_2O_3$ samples

Synthetic mixture	Chem. comp. (wt.%)			Metallic nickel (wt.%)	
	Ni	NiO	Al_2O_3	Chemical method	Thermal method
1	0	15.0	85.0	0	0
2	5.0	15.0	80.0	5.06	5.07
3	10.0	10.0	80.0	9.95	10.02
4	15.0	5.0	80.0	14.85	14.97

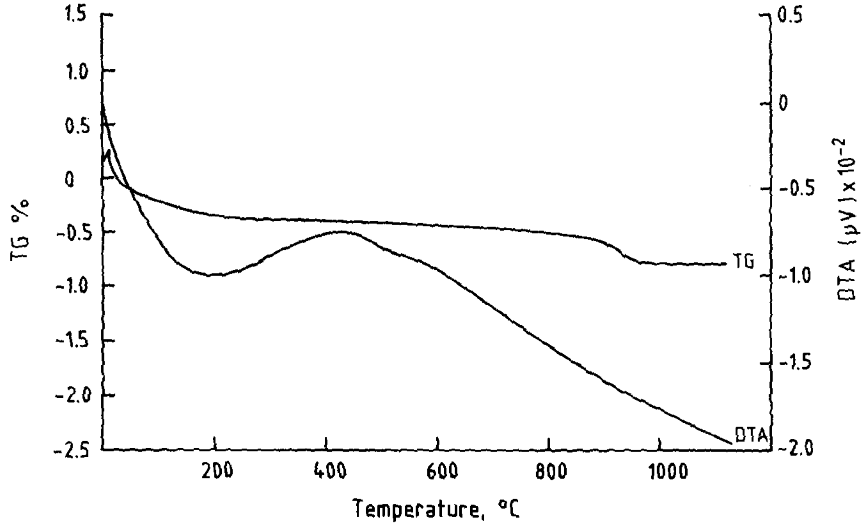

Fig. 1. Thermogram of fresh steam-re-forming catalyst (type A, Ni = 20.3%).

the following reaction [11]

$$\mathrm{Ni} + \tfrac{1}{2}\mathrm{O_2} \rightarrow \mathrm{NiO} \qquad \Delta H^{\ominus}_{298} = -57.46\ \mathrm{kcal\ mol^{-1}}$$

This reaction, especially in the case of finely dispersed nickel, is very rapid and has an important thermal colouration. During thermal analysis, the metallic nickel produced from nickel oxide during the reduction period is re-oxidised by oxygen in the thermal analyser.

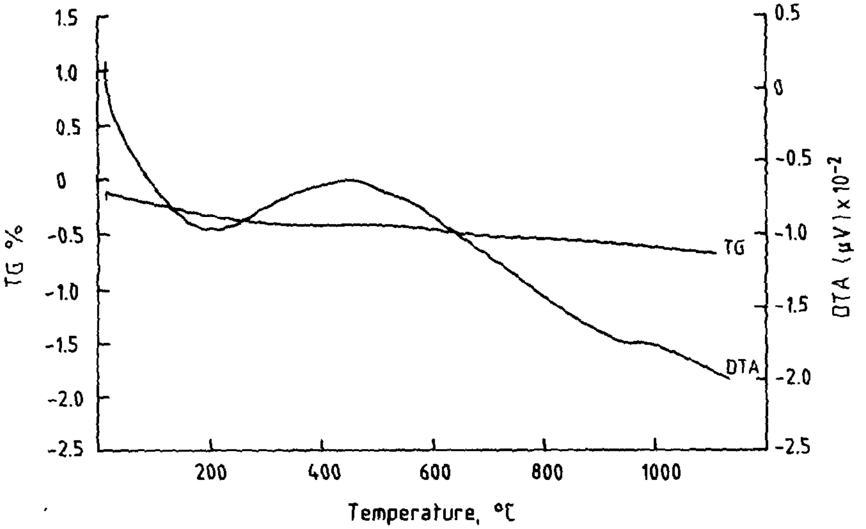

Fig. 2. Thermogram of fresh steam-re-forming catalyst (type B, Ni = 12.8%).

TABLE 4

Extent of reduction by thermal analysis techniques

Run	T_{max} of oxidation peak (°C)	Weight gain (%)	Metallic nickel (%)	Extent of reduction (%)
1	440	5.57	21.12	98.7
2	455	6.02	22.03	102.9
3	415	3.39	12.41	91.9
4	415	3.47	12.70	94.1
5	418	3.55	12.99	96.2
6	465	3.63	13.29	98.4
7	438	5.52	20.20	94.4
8	455	5.75	21.05	98.4
9	450	5.45	19.95	93.2
10	445	5.50	20.13	94.1
11	450	5.50	20.13	94.1
12	440	5.60	20.50	95.8
13	420	3.60	13.18	97.6
14	410	3.65	13.36	99.0
15	400	5.25	19.22	89.8
16	445	5.59	20.46	95.6
17	370	3.43	12.55	93.0
18	410	3.78	13.83	102.4
19	415	3.72	13.62	100.9
20	405	5.13	18.78	87.8
21	445	5.99	21.90	102.3
22	422	3.72	13.62	100.9
23	375	3.38	12.37	91.6
24	450	6.02	22.03	102.9
25	410	5.44	19.91	93.0
26	425	5.77	21.12	98.7
27	405	4.55	17.75	82.9
28	420	3.71	13.58	100.6

All the reduced catalyst samples (Table 4) exhibited an exothermic effect with a T_{max} value in the temperature range 375–465°C and a corresponding weight gain [15,16]. The oxidation of metallic nickel present in the samples started at 200°C and was complete at 700°C.

The weight gain in the temperature range 200–700°C was used to calculate the amount of metallic nickel present in the sample and, hence, the extent of reduction. The weight gain was in the range of 3.4–6.0 wt.% corresponding to a metallic nickel content of 12.4–22.0%. Thermal analysis gives the net effect of weight and thermal changes. In calculating the metallic nickel content, it was assumed that the net weight gain reflects only the weight change resulting from the oxidation of metallic nickel. Thus, any weight changes that occur in addition to nickel oxidation, decrease the accuracy of the metallic nickel content determination.

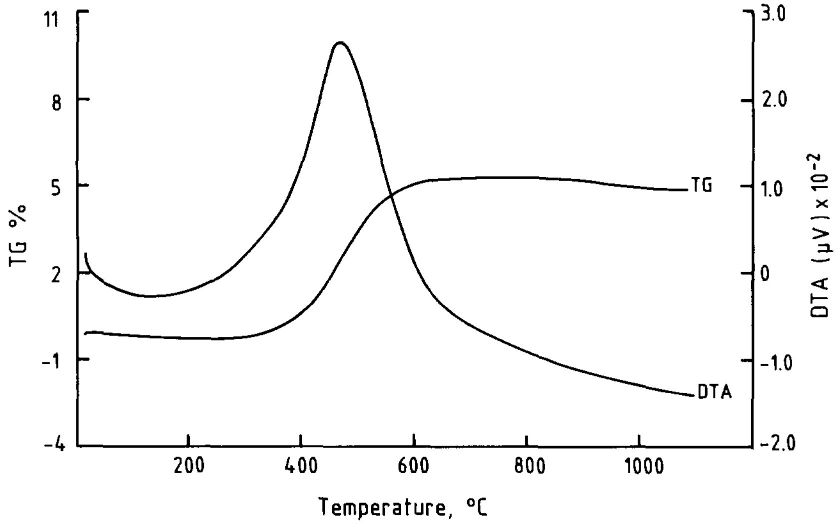

Fig. 3. Thermogram of reduced steam-re-forming catalyst (type A, Ni = 20.3%).

The metallic nickel, total nickel and the extent of reduction of the reduced catalyst samples, as determined by the longer, and time-consuming chemical analysis method, are presented in Table 5. The results of both the thermal and chemical analyses indicated essentially complete reduction ($>$ 95%) for runs with reduction temperatures greater than 300°C. A few of the experiments at 300°C, depending on the reduction duration and space velocity, indicated partial but still substantial reduction of the catalyst ($>$ 88%).

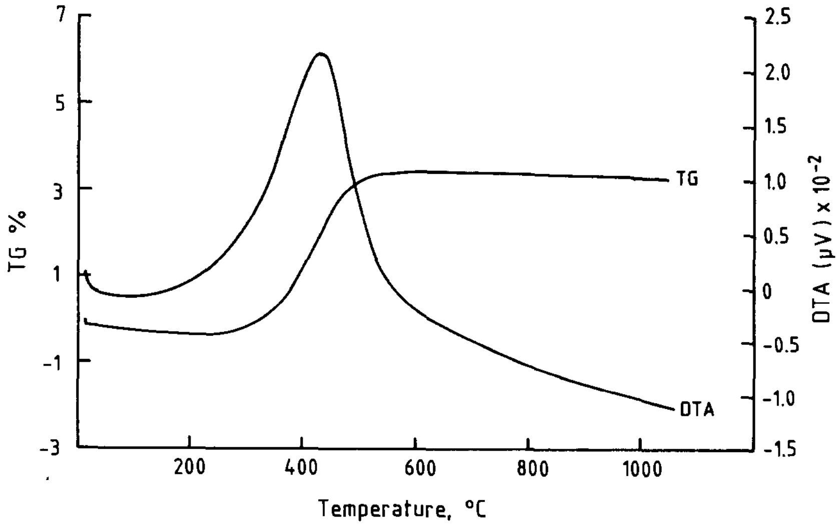

Fig. 4. Thermogram of reduced steam-re-forming catalyst (type B, Ni = 12.8%).

TABLE 5

Extent of reduction by chemical analysis method

Run	Metallic Ni (wt.%)	Total Ni (wt.%)	Extent of Reduction (%)
1	20.8	21.6	95.4
2	21.8	21.9	99.5
3	13.0	13.1	99.2
4	13.2	13.3	99.2
5	13.5	13.5	100.0
6	13.7	13.7	100.0
7	20.6	21.6	95.3
8	21.7	21.7	100.0
9	22.0	22.0	100.0
10	21.9	21.8	100.5
11	21.6	21.9	98.6
12	22.3	22.2	100.5
13	14.6	14.4	101.4
14	13.5	13.5	100.0
15	20.7	21.8	95.0
16	22.3	22.3	100.0
17	13.2	14.2	93.0
18	14.4	14.5	99.3
19	14.0	14.0	100.0
20	21.0	22.0	95.5
21	22.4	22.6	99.1
22	13.8	13.8	100.0
23	13.8	13.8	100.0
24	22.1	22.0	100.5
25	21.2	21.5	98.6
26	22.3	22.4	99.6
27	19.3	22.0	87.7
28	14.2	14.3	99.3

The trends and magnitudes of the extent of reduction measured by thermal analysis were consistent with the chemical analyses. The maximum and average differences in absolute values of the % extent of reductions determined by the two methods were about 8% and 3%, respectively. Given the overall estimated experimental error (reduction plus analysis) of about 5% in the extent of reduction determination, it may be concluded that the results of the two methods compare quite well.

The metallic nickel and total nickel contents of the reduced catalyst were determined by chemical analysis on a dry basis; therefore, some of the values of total nickel (Table 5) are greater than the 12.8 and 20.3 wt.% Ni determined for the fresh catalysts (Table 1). The determination of the extent of reduction by thermal analysis requires, in addition to the metallic nickel, a knowledge of the total nickel content. In order to compare the results on the same dry basis, the total moisture lost up to the reduction temperature is needed in order to determine the moisture-free nickel content of the reduced catalyst. This should then be used as the denominator in the calculation of the extent of reduction.

The thermal analysis of the fresh catalysts gave a total weight loss of about 0.5% over the temperature range 20–1000°C due to the loss of moisture. This implies, from the chemical analysis of the fresh catalysts, that the two catalysts studied contained about 13.5 and 21.4 wt.% total nickel on a dry basis. These were the numbers used as denominators in calculating the extent of reduction by thermal methods (Table 4). It is worth noting that the change in weight of only 0.5% due to loss of moisture translates to about 5.5% change in the wt.% of total nickel in the catalyst, as well as the corresponding extent of reduction.

The above discussion clearly indicates that within an acceptable difference/error of about 5%, the results of the rapid thermal analysis technique compare quite well with the more tedious, time-consuming chemical analysis. Thermal analysis may therefore be used as a tool for the rapid determination of the extent of reduction of reduced steam-re-forming catalysts.

CONCLUSIONS

DTA and TG analyses can be used as rapid methods to determine the extent of reduction of supported steam-re-forming catalysts. The reduced steam-re-forming catalysts, over the temperature range 20–1000°C, were thermally stable and were characterised by one exothermic peak (the oxidation of metallic nickel) with a corresponding gain in weight.

ACKNOWLEDGMENTS

The authors acknowledge the support of the Research Institute, King Fahd University of Petroleum and Minerals and King Abdulaziz City for Science and Technology (Research Grant No. AR-9-064) in conducting this research.

REFERENCES

1 N. Pernicone and F. Triana, Pure Appl. Chem., 50 (1978) 1169–1191.
2 K. Mok, J.R.H. Ross and R.M. Sambrook, Preparation of Catalysts, Vol. III, Elsevier, Amsterdam, 1983, p. 291.
3 D. Blackmond and E.I. Ko, Appl. Catal., 13 (1984) 49–68.
4 W. Keely and H.W. Maynor, J. Chem. Eng. Data, 8 (1963) 297.
5 J.R. Rostrup-Nielsen, J. Catal., 27 (1972) 343.
6 K. Kinson, J.E. Dickenson and C.B. Belcher, Anal. Chim. Acta, 41 (1968) 107–112.
7 T.Y. Tynlikora, Zavod. Lab., 36 (1970) 1038–1040.

8 H. Swift, F. Lutinski and W.L. Kehl, J. Phys. Chem., 69 (1965) 3268–3274.
9 H. Swift, F. Lutinski and H. Tobin, J. Catal., 5 (1966) 285–292.
10 C.H. Bartholomew and R.J. Farrauto, J. Catal., 45 (1976) 41–53.
11 J. Macak and J. Malecha, Anal. Chem., 41 (1969) 442–446.
12 D. Dollimore, Thermochim. Acta, 50 (1981) 123–126.
13 G.C. Bond and M. Gelsthorpe, Thermal. Anal. Abs., 14 (1985) 205–208.
14 F. Janssen, Thermochim. Acta, 148 (1989) 137–147.
15 Y.D. Yeboah and A. Aitani, Thermochim. Acta, 149 (1989) 147–156.
16 G. Rasulic, L. Milanovic and S. Jovanic, J. Them. Anal., 30 (1985) 73–82.
17 Z. Marzenko, Spectrophotometric Determination of Elements, Ellis Horwood, Amsterdam, 1976, 291.
18 ASTM Metal Test Methods and Analytical Procedures, Annual Books of ASTM Standards, Vol. 3.05, ASTM, Philadelphia, PA, USA, 1983.