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Study on the regeneration of deactivated NiO/γ-Al_2O_3 catalyst for the conversion of natural gas with CO_2 to synthesis gas by TG[☆]

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Abstract

Thermogravimetry was used to follow the oxidation–reduction as well as the regeneration processes of deactivated NiO/γ-Al_2O_3 catalysts. The results indicate that the catalysts, whose deactivation was caused by the sintering of metallic Ni and by the forming of $NiAl_2O_4$ species, could be regenerated through a reduction–oxidation method. Especially, the regeneration of $NiAl_2O_4$ to NiO was more than 90%. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: NiO/γ-Al_2O_3 catalyst; Deactivation; Regeneration; TG

1. Introduction

NiO/γ-Al_2O_3 is an excellent catalyst for many catalytic reactions. Usually, the deactivation of the catalyst was considered to be through two different ways: one is coke deposition, which is regarded as a temporary deactivation [1], while the other is the sintering of metallic Ni and the formation of a $NiAl_2O_4$ species, which is considered to be a permanent deactivation. However, it was reported that it is possible to regenerate the deactivated catalysts caused by the formation of $NiAl_2O_4$ [2].

In this paper, the behaviors of oxidation–reduction of a deactivated catalyst was first examined by the thermogravimetry (TG) technique, and the amounts of NiO and $NiAl_2O_4$ on the catalyst were calculated from the corresponding mass-loss in the reduction process. Then, the regeneration process of the deactivated catalyst caused by sintering of metallic Ni and by forming of $NiAl_2O_4$ with reduction–oxidation method was investigated. The regeneration percent of $NiAl_2O_4$ to NiO was calculated from the amount of NiO included in $NiAl_2O_4$ before oxidation and the amount of NiO formed after oxidation.

These data are necessary for the selection of optimal regeneration conditions and the design of the regeneration reactor.

2. Experimental

2.1. Catalyst preparation and reaction tests

The NiO/γ-Al_2O_3 catalyst was prepared by impregnating γ-Al_2O_3 with the corresponding aqueous solution of $Ni(NO_3)_2{\cdot}6H_2O$, dried and calcined at 450°C

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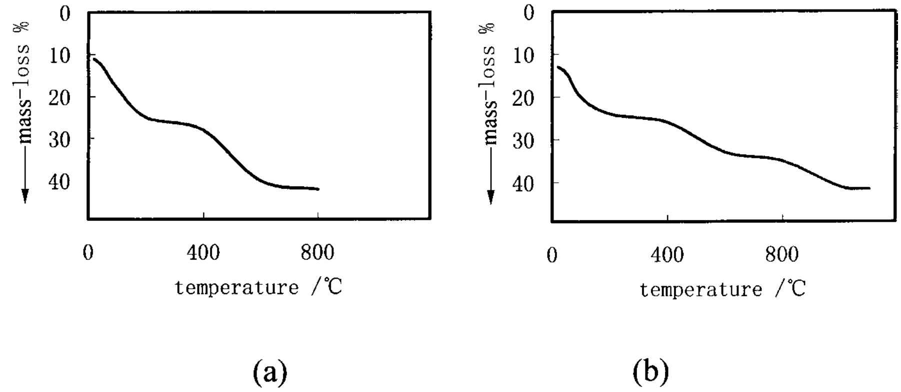

Fig. 1. TG curves of the first oxidation (a) and reduction (b) of Cat(750-260).

for 4 h in air. The catalyst was tested at 750°C and 850°C, respectively, for 260 h. The catalysts are then designated as Cat(750-260) and Cat(850-260), respectively.

2.2. *Reaction gases*

The oxidation gas used was air, and the reduction gas was H_2.

2.3. *Oxidation–reduction measurements*

Oxidation–reduction measurements were performed on the thermobalance of a Shimadzu DT-30 type thermoanalyzer with 2–5 mg range, heating rate 10 K min^{-1}, and chart speed 1.25 mm min^{-1}.

3. Results and discussion

3.1. *First oxidation–reduction behaviors of deactivated catalysts*

In order to investigate the regeneration of a deactivated catalyst, TG was first used to follow its oxidation–reduction process. Figs. 1 and 2 show the first oxidation–reduction TG curves of Cat(750-260) and Cat(850-260) in air–H_2, respectively.

It can be seen from Fig. 1(a) and Fig. 2(a) that the oxidation behaviors of Cat(750-260) and Cat(850-260) are not quite the same. There are two mass-loss stages in the oxidation TG curve of Cat(750-260), the first mass-loss stage (40–150°C) corresponds to desorption of free water on the catalyst, while the

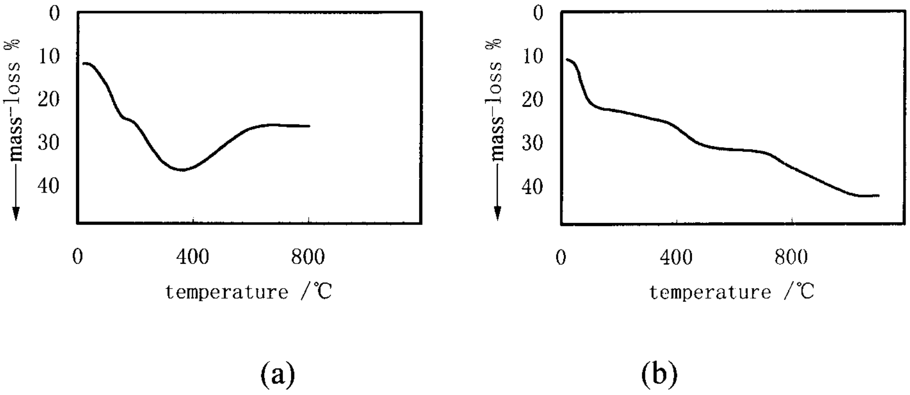

Fig. 2. TG curves of the first oxidation (a) and reduction (b) of Cat(850-260).

Table 1
TG reduction results of deactivated catalysts

Catalyst	Sample mass (mg)	Reduction of NiO (340–480°C)			Reduction of $NiAl_2O_4$ (760–930°C)		
		Mass-loss	NiO		Mass-loss	$NiAl_2O_3$	
		(mg)	(mg)	(%)	(mg)	(mg)	(%)
Cat(750-260)	40.85	0.225	1.05	2.57	0.425	4.69	11.48
Cat(850-260)	40.30	0.400	1.86	4.61	0.600	6.62	16.43

second mass-loss stage (335–800°C) can be attributed to the combustion of the coke on the catalyst. However, in the oxidation TG curve of Cat(850-260) a mass-loss stage and a mass-gain stage were observed. The mass-loss stage (40–150°C) corresponds to adsorption of free water as well. The mass-gain stage (340–500°C) can only be attributed to the oxidation of sintered Ni, but not to combustion of coke on the catalyst, because the reaction temperature of 850°C is not in the temperature range of coke formation [3]. However, it can be found from Fig. 1(b) and Fig. 2(b) that their reduction behaviors after oxidation are very similar, i.e., they all have two mass-loss stages in the TG curves of reduction besides the mass-loss stage (40–150°C) of free water. The first mass-loss stage (340–480°C) and the second mass-loss stage (760–930°C) obviously correspond to the reduction of NiO and $NiAl_2O_4$, respectively. The amounts of NiO and $NiAl_2O_4$ can be calculated from the corresponding mass-loss of reduction, as shown in Table 1.

The results in Table 1 show that the amount of supported NiO for the Cat(750-260) is less than that for Cat(850-260), and this is because there is coke formation on Cat(750-260), and a part of the supported NiO was sintered during the combustion of coke. The results in Table 1 also show that the amount of $NiAl_2O_4$ on the Cat(750-260) is also less than that on the Cat(850-260), and this is due to the fact that the reaction temperature of the former is considerably less than that of the latter.

3.2. Second oxidation–reduction behaviors of deactivated catalysts

Figs. 3 and 4 show the second oxidation–reduction TG curves of Cat(750-260) and Cat(850-260) in air–H_2, respectively.

It can be found from Figs. 3 and 4 that the two deactivated catalysts have similar second oxidation–reduction TG curves. In the second oxidation TG curves (a) a mass-loss stage and a mass-gain stage

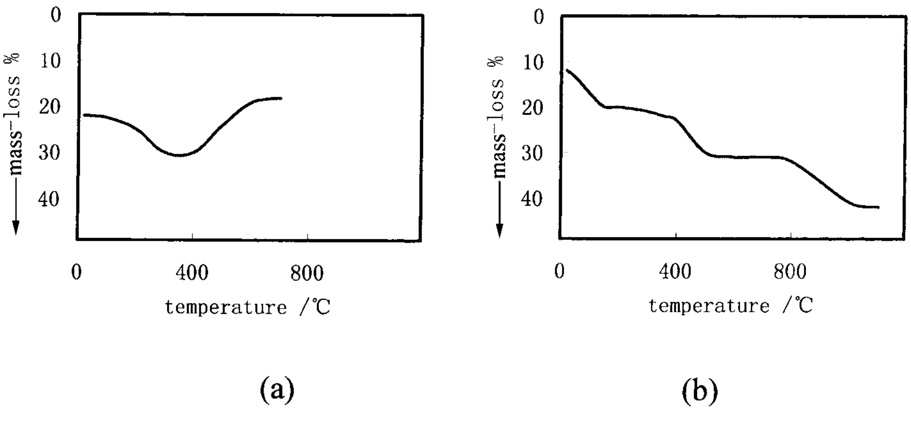

Fig. 3. TG curves of the second oxidation (a) and reduction (b) of Cat(750-260).

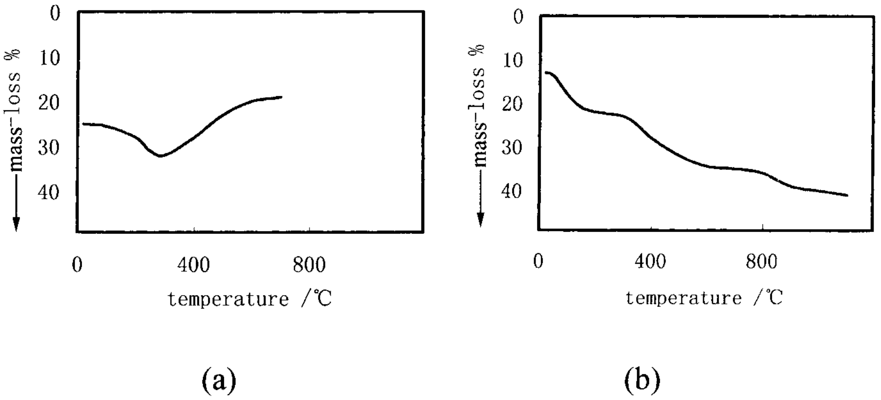

Fig. 4. TG curves of the second oxidation (a) and reduction (b) of Cat(850-260).

can be observed, the mass-loss stage (40–150°C) corresponds to desorption of free water on the catalyst, the mass-gain stage (300–500°C) is due to oxidation of sintered Ni, and in the second reduction TG curves (b) two mass-loss stages can be observed besides the mass-loss stage (40–150°C) of free water. Mass-loss stage (340–480°C) and (760–930°C) are due to reduction of NiO and $NiAl_2O_4$, respectively. The amount of NiO and $NiAl_2O_4$ can also be calculated from corresponding reduction mass-loss. The results are listed in Table 2 and are compared with results of first reduction, as shown Table 3.

It can be found from Table 3 that the amount of NiO on the catalysts after second oxidation are higher than that on the catalysts after first oxidation. It may be one of the reasons that metallic Ni sintered in the first reduction process was again oxidized to NiO in the second oxidation process. It can also be found that the amount of $NiAl_2O_4$ on catalysts after second oxidation are less than that on catalysts after the first oxidation process. This can be confirmed by following the oxidation–reduction behaviors of the catalysts calcined at high temperatures. Therefore, the total amount of NiO on the catalysts after second oxidation

Table 2
Second TG reduction results of deactivated catalysts

Catalyst	Sample mass (mg)	Reduction of NiO (340–480°C)			Reduction of $NiAl_2O_4$ (760–930°C)		
		Mass-loss	NiO		Mass-loss	$NiAl_2O_4$	
		(mg)	(mg)	(%)	(mg)	(mg)	(%)
Cat(750-260)	39.47	0.500	2.33	5.90	0.225	2.48	6.28
Cat(850-260)	38.35	0.650	3.03	7.90	0.260	2.87	7.48

Table 3
Comparison of amounts of supported NiO and $NiAl_2O_4$

Catalyst	After first oxidation		After second oxidation	
	NiO (%)	$NiAl_2O_4$ (%)	NiO (%)	$NiAl_2O_4$ (%)
Cat(750-260)	2.57	11.48	5.9	6.28
Cat(850-260)	4.61	16.43	7.90	7.48

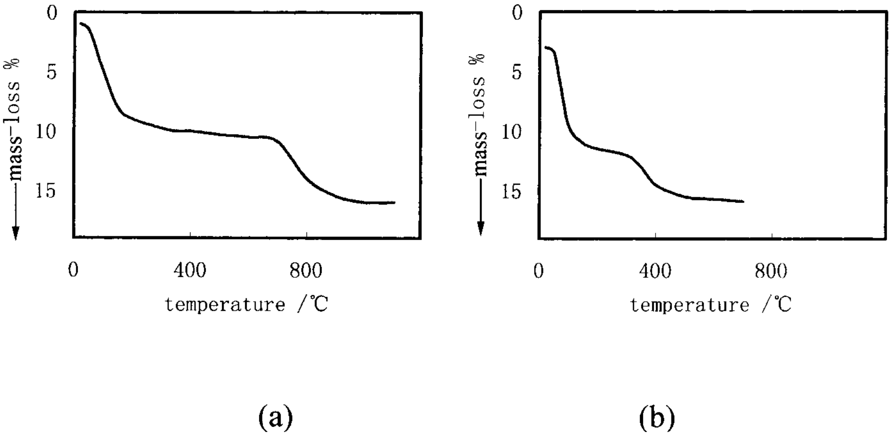

Fig. 5. TG curves of first reduction (a) and second reduction (b) of $NiAl_2O_4/\gamma\text{-}Al_2O_3$ catalyst.

includes: (i) unsintered NiO, (ii) NiO yielded by the second oxidation of sintered Ni which was formed from NiO in the first reduction process, and (iii) NiO obtained from the second oxidation of sintered Ni which was formed by $NiAl_2O_4$ in the first reduction process. Thus, it can be concluded that catalysts deactivation caused by the sintering of metallic Ni formed by NiO and $NiAl_2O_4$ in the reduction process can be regenerated by repeating the reduction–oxidation method.

3.3. Reduction behavior of the $NiAl_2O_4/\gamma\text{-}Al_2O_3$ catalyst

In order to further confirm the fact that the $NiAl_2O_4$ species on the catalysts can be changed into NiO, TG was used again to follow the reduction process of the $NiAl_2O_4/\gamma\text{-}Al_2O_3$ catalyst obtained by calcining at 1100°C. Fig. 5 shows the first reduction TG curve (a) and the second reduction TG curve (b) of the $NiAl_2O_4/\gamma\text{-}Al_2O_3$ catalyst.

It is clear that both the behaviors of first reduction and second reduction for the $NiAl_2O_4/\gamma\text{-}Al_2O_3$ catalyst is not quite the same.

There is only a mass-loss stage in their reduction TG curves besides the mass-loss stage corresponding to free water. The mass-loss stage in the TG curve of first reduction (a) appears in the 760–970°C range and is obviously caused by the reduction of $NiAl_2O_4$. This implies that all supported NiO can change to $NiAl_2O_4$ under the condition of high temperatures. But the mass-loss stage in the TG curve of the second reduction (b) appears in the 340–460°C range and is obviously caused by reduction of NiO. This shows that all $NiAl_2O_4$ was again changed to NiO under certain conditions. The results of the two reductions of the $NiAl_2O_4/\gamma\text{-}Al_2O_3$ catalyst are listed in Table 4.

The results in Table 4 show that the $NiAl_2O_4$ formed at high temperatures can be converted to NiO by the reduction–oxidation method. The conversion or regeneration percent is more than 90%. It is enough to prove that catalyst deactivation caused by forming

Table 4
The results of two reductions of the $NiAl_2O_4/\gamma\text{-}Al_2O_3$ catalyst

Sample mass (mg)	First reduction (760–970°C)		Second reduction (340–460°C)		Conversion (%)
	Mass-loss (mg)	NiO in $NiAl_2O_4$ (mg)	Mass-loss (mg)	NiO (mg)	
16.35	0.385	1.79	0.35	1.63	91

$NiAl_2O_4$ species can be regenerated through the reduction–oxidation method.

4. Conclusion

The TG technique can be used to investigate regeneration of deactivated NiO/γ-Al_2O_4 catalysts. The results of oxidation–reduction of deactivated catalysts show that both the deactivation caused by sintering of metallic Ni formed from NiO and $NiAl_2O_4$ in the reduction process and the deactivation caused by the forming of $NiAl_2O_4$ species on NiO/γ-Al_2O_3 catalysts can be regenerated through the reduction–oxidation method.

References

[1] J.B. Claridge, M.L.H. Green, S.C. Tsang, A.P.E. York, A.T. Ashcroft, P.D. Battle, Catal. Lett. 22 (1993) 299.

[2] Fan Yemei, Xu Hengyong, Zhou Peiheng, Natural Gas Chemical Industry, C_1 Chemistry Chem. Eng. 2 (1995) 6.

[3] A.M. Gadalla, B. Bower, Chem. Eng. Sci. 1 (1988) 3049.