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A STUDY OF THE EFFECT OF CALCINATION TEMPERATURE ON THE INTERACTION BETWEEN THE ACTIVE COMPONENT AND THE CARRIER OF A CATALYST USING THERMOANALYSIS AND X-RAY DIFFRACTION

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ABSTRACT

The reduction behaviour under hydrogen of nickel catalysts supported on Al_2O_3, Nb_2O_5, TiO_2 and ground glass carriers has been studied by thermoanalysis. The results show that the active component, NiO, interacts with Nb_2O_5 to form $NiNb_2O_6$ at 400 °C, and at 900 °C NiO interacts with Al_2O_3 and TiO_2 to form $NiAl_2O_4$ and $NiTiO_3$ respectively. The existence of the above-mentioned Support–Metal Strong Interaction (SMSI) was verified by in situ X-ray diffraction analysis. In the case of NiO/glass calcined at 900 °C a new phase was formed; its composition has yet to be determined.

INTRODUCTION

The effective surface of the metal component of a catalyst can be increased by dispersing it on a support, this being regarded as an inert substance [1,2]. Numerous experiments have shown, however, that the support is not inert. The metal component and the support interact and even form some new compounds. In 1978 Tauster and coworkers [3–5] found that the adsorption capacities for H_2 and CO of Ru, Rh, Pd, Os, Ir and Pt supported on TiO_2 treated with hydrogen at high temperature are much lower than when treated at low temperature. According to traditional theories, the sintering of metal at high temperature may cause the decrease in adsorbability, but neither crystal growth not sintering have been found by X-ray diffraction analysis. Thus, the concept of Support–Metal Strong Interaction (SMSI) was proposed to explain the above-mentioned phenomena. Because of the SMSI, the catalysts have different catalytic properties [6–14], which, in particular, has an important effect on the behaviour of redox-type catalytic reactions. Thus, studies of SMSIs are of undoubtedly

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important and wide ranging significance in the understanding of catalysts and catalysis, and in enhancing the catalytic properties of catalysts by modifying the SMSIs.

In recent years, SMSI study has achieved further development following the application of modern physical measurement techniques. Numerous investigations have shown that SMSI depends not only on the metal and support themselves, but also on the dispersion of the metal and on the catalyst preparation conditions, such as calcination temperature and reduction. In this work, starting with the calcination of catalysts, we have studied the reduction behaviour of nickel catalysts supported on Al_2O_3, Nb_2O_5, TiO_2 and ground glass carriers using thermoanalysis to delineate the mechanism of SMSI. In addition, the existence of SMSI was verified by in situ X-ray diffraction. Some valuable information concerning the improvement of nickel catalysts has also been obtained.

EXPERIMENTAL

Catalyst samples

The catalysts investigated were 9% NiO/Al_2O_3, 12.5% NiO/Nb_2O_5, 13% NiO/TiO_2 and 3.8% NiO/glass.

Apparatus and requirements

The calcination and reduction of the catalysts were carried out on an attached TG–DTG unit of a Shimadzu DT-20B type thermoanalyser with the following experimental conditions: measuring range, 2–10 mg; heating rate, 10 °C min^{-1}; and paper speed, 1.25 mm min^{-1}.

XRD analysis was carried out on a Rigaku D/max IIIB X-ray diffractometer: Cu $K\alpha$, 40 kV, 50 mA (Ni filter), scanning rate 2 deg min^{-1}.

RESULTS AND DISCUSSION

Reduction of calcined NiO/Al_2O_3 under H_2

TG–DTG curves of NiO/Al_2O_3 calcined at 400 and 900 °C and reduced in H_2 are given in Fig. 1; their X-ray diffraction patterns are shown in Fig. 2.

Figure 1 shows that two peaks appear in the DTG curve of NiO/Al_2O_3 calcined at 400 °C, the relevant weight loss being observed in the corresponding TG curve. The first peak is the desorption of H_2O from the surface. The second peak is in the range 320–640 °C with a peak tempera-

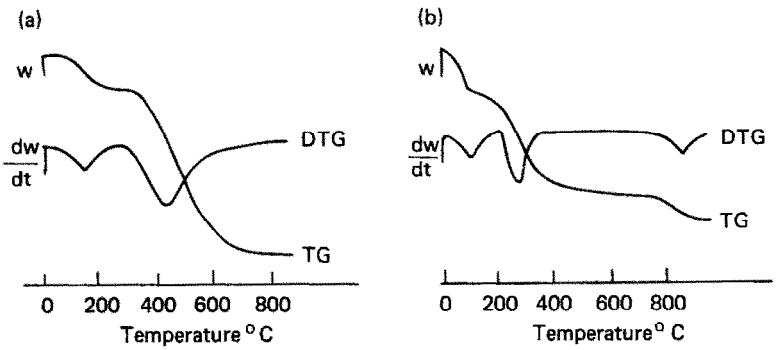

Fig. 1. TG–DTG curves of NiO/Al_2O_3 catalyst reduced by H_2: (a), sample calcined at 400 °C; (b), sample calcined at 900 °C.

ture of 430 °C and shows the reduction of NiO. In comparision with the reduction of single component NiO, the temperature range of the reduction has shifted backwards and the weight loss far exceeds the theoretical. This is due to the weight loss of NiO by reduction and also the loss of hydroxyl group on Al_2O_3. There is no obvious change in the TG–DTG curve above 640 °C.

XRD patterns reveal the presence of a very fine $NiAl_2O_4$ crystal phase but the diffraction peak is diffuse, demonstrating that only a little active metal component forms $NiAl_2O_4$ with Al_2O_3, and that most of the active component is still in the form of NiO.

Three peaks appear in the DTG curve of NiO/Al_2O_3 calcined at 900 °C, the corresponding TG curves showing the relevant weight loss. The first peak indicates the desorption of surface water; the second is in the range 205–340 °C, with the peak at 260 °C, indicating the reduction of NiO; the third occurs over the range 742–950 °C with the peak at 846 °C and is

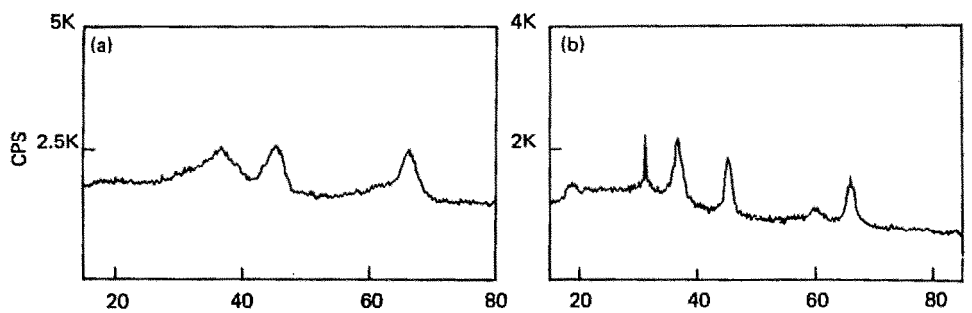

Fig. 2. XRD patterns of NiO/Al_2O_3 catalyst: (a), sample calcined at 400 °C; (b), sample calcined at 900 °C.

TABLE 1

Ni content of NiO/Al_2O_3 determined by thermogravimetry and chemical analysis

Reaction	Weight loss (mg)	Ni content (mg)	Ni (%)		
			TG	Total	Chemical analysis
Reduction of NiO	0.298	1.09	5.2	8.4	9
Reduction of $NiAl_2O_4$	0.298	0.667	3.2		

Sample weight 20.77 mg.

expected to represent the reduction of $NiO \cdot Al_2O_3$ (the SMSI product of NiO and Al_2O_3). The reduction reactions are

$$NiO + H_2 \rightarrow Ni + H_2O \quad (1)$$

$$NiAl_2O_4 + H_2 \rightarrow Ni + Al_2O_3 + H_2O \quad (2)$$

and the Ni content calculated from the weight loss by reduction is compared with the results of chemical analyses in Table 1. It can be seen that the total Ni content calculated from the weight loss of NiO and $NiAl_2O_4$ by reduction is basically consistent with the analytical result; thus, the third peak can be assigned as the reduction of $NiAl_2O_4$.

XRD patterns show that $NiAl_2O_4$ is the main phase, demonstrating that most of the active component, NiO, and Al_2O_3 carrier form a new spinel compound, nickel aluminate, through SMSI.

Reduction of calcined NiO/Nb_2O_5 under H_2

TG–DTG curves of NiO/Nb_2O_5 (calcined at 450 and 900 °C) reduced in H_2 are shown in Fig. 3 and their XRD patterns are illustrated in Fig. 4. There are two peaks in the DTG curve (Fig. 3) of the NiO/Nb_2O_5 catalyst calcined at 450 °C, with no peak for NiO reduction: The first is the

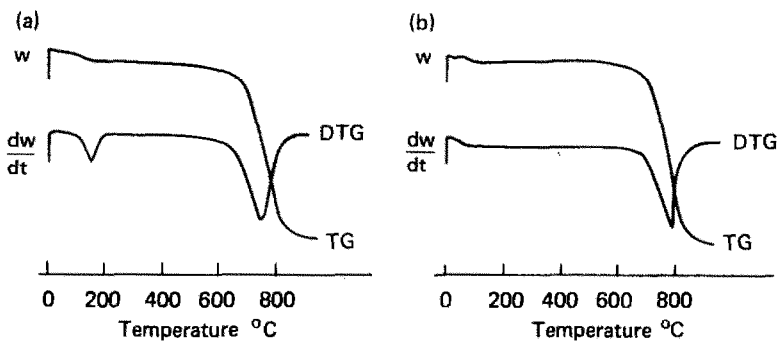

Fig. 3. TG–DTG curves of NiO/Nb_2O_5 catalyst reduced by H_2: (a), sample calcined at 450 °C; (b), sample calcined at 900 °C.

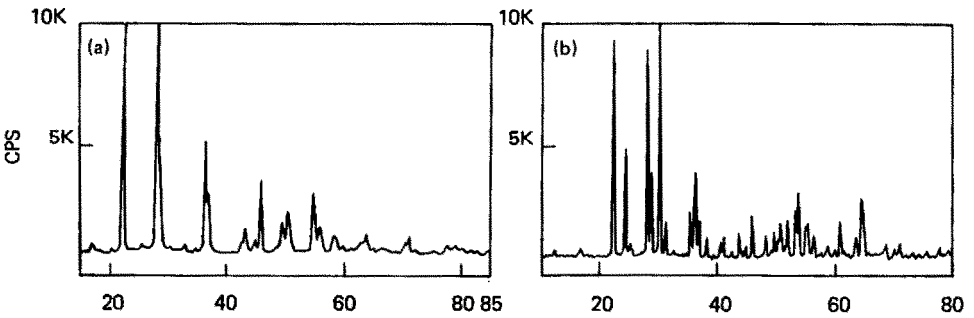

Fig. 4. XRD patterns of NiO/Nb_2O_5 catalyst: (a), sample calcined at 450 °C; (b), sample calcined at 900 °C.

desorption of surface water; the second, in the range 623–810 °C with the peak at 775 °C, may be the reduction of $NiO \cdot Nb_2O_5$ (the product of NiO and Nb_2O_5 via SMSI). Assuming the reduction of $NiO \cdot Nb_2O_5$ is as follows

$$NiO \cdot Nb_2O_5 + H_2 \rightarrow Ni + Nb_2O_5 + H_2O \quad (3)$$

$$NiO \cdot Nb_2O_5 + 3H_2 \rightarrow Ni + Nb_2O_3 + 3H_2O \quad (4)$$

the Ni content calculated from weight loss by reduction is compared with the results of chemical analysis in Table 2. The results calculated according to reactions (3) and (4) are not in agreement with those obtained by chemical analysis; this may be because the supposed reduction product is not rational.

The XRD patterns show the presence of an $NiNb_2O_6$ phase, the new compound formed between NiO and Nb_2O_5 by SMSI.

In the DTG curve of the reduced sample calcined at 900 °C, there is only one peak present in the range of 650–820 °C, the peak temperature being 770 °C; the relevant weight loss is observed in the corresponding TG curve. Obviously, it is due to the reduction of the SMSI product $NiO \cdot Nb_2O_5$. The Ni contents calculated according to reactions (3) and (4) are compared with those of the sample calcined at 450 °C in Table 3. The results show that the Ni contents calculated for the sample calcined at 900 °C are higher than for those calcined at 450 °C.

TABLE 2

Ni content of NiO/Nb_2O_5 determined by thermogravimetry and chemical analysis

Reaction	Weight loss (mg)	Proportion of weight loss		Ni content (mg)	Ni (%)	
		NiO	Nb_2O_5		TG	Chemical analysis
Eqn. (3)	1.67	1	0	6.12	18.6	12.5
Eqn. (4)		1/3	2/3	2.04	6.2	

Sample weight 32.9 mg.

TABLE 3

Ni content of NiO/Nb_2O_5 catalyst

Sample weight (mg)	Calcination temperature (°C)	Reaction	Ni content	
			(mg)	(%)
32.9	450	Eqn. (3)	6.12	18.6
		Eqn. (4)	2.04	6.2
28.2	900	Eqn. (3)	5.50	19.5
		Eqn. (4)	1.8	6.5

The same $NiNb_2O_6$ phase is observed in the XRD pattern of the sample calcined at 900 °C, it being present in slightly higher amounts than in the sample calcined at 450 °C, showing that although $NiNb_2O_6$ phase is present at 450 °C, its formation is more complete at 900 °C.

Reduction of calcined NiO/TiO_2 under H_2

The TG–DTG curves of NiO/TiO_2 (calcined at 400 and 900 °C) reduced in H_2 are given in Fig. 5, and their XRD patterns are shown in Fig. 6.

Figure 5 shows that there are five peaks on the DTG curve of NiO/TiO_2 calcined at 400 °C and the relevant weight loss is observed on their corresponding TG curves. The first and second peaks appearing below 160 °C show the desorption of surface water. Because the carrier is composed of two crystal types of TiO_2 (rutile : anatase = 30 : 70), there are two dehydration temperatures. The overlapping peaks (310 and 420 °C) are in the range 273–560 °C, which may correspond to the reduction of NiO on the two types of TiO_2 carrier. In order to confirm this, the total amount of Ni calculated from weight loss by reduction is compared with that determined by chemical analysis in Table 4. The calculated Ni content is slightly lower than that determined, because of the non-uniform nature of the sample, and

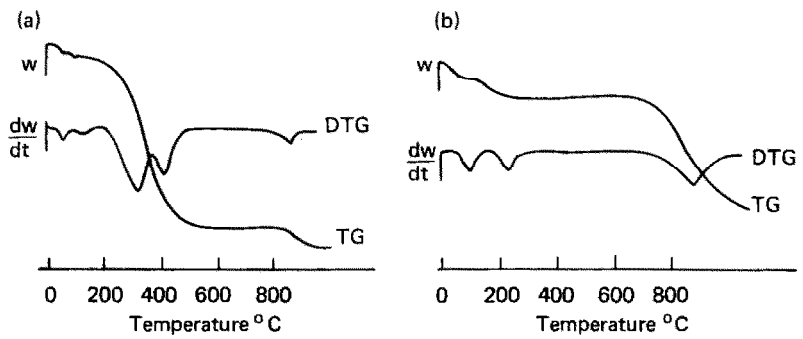

Fig. 5. TG–DTG curves of NiO/TiO_2 catalyst reduced by H_2: (a), sample calcined at 400 °C; (b), sample calcined at 900 °C.

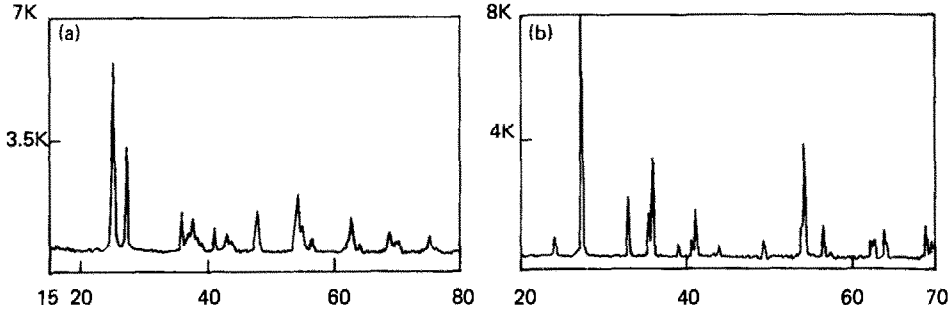

Fig. 6. XRD patterns of NiO/TiO_2 catalyst: (a), sample calcined at 400 °C; (b), sample calcined at 900 °C.

shows that the active component has not interacted with the TiO_2 and remains in the form of NiO. The fifth peak appears above 800 °C and is assigned to the reduction of TiO_2 by comparision with the TG–DTG curve of single component TiO_2 reduced in H_2.

The XRD patterns show the existence of anatase and rutile with the former predominant; there is no interaction between the active component, NiO, and the two types of TiO_2 carrier.

There are three peaks present in the TG–DTG curve of the reduced NiO/TiO_2 sample calcined at 900 °C, and the relevant weight loss is seen on the corresponding TG curve. The first two peaks, below 200 °C, show the desorption of surface water on the two types of TiO_2; the peak temperatures are higher than those of the sample calcined at 400 °C. The third peak appears above 750 °C, about 50 °C lower than the reduction temperature of single component TiO_2, and is regarded as the reduction of $NiO \cdot TiO_2$, the product of the interaction of NiO with TiO_2. The continual weight loss observed up to 900 °C, may include the reduction of TiO_2.

The XRD pattern in Fig. 6b illustrates the disappearance of the anatase phase, part of this being transformed to rutile, and the simultaneous formation of the new phase, $NiTiO_3$, a spinel produced by the reaction of NiO with rutile.

TABLE 4

Ni content of NiO/TiO_2 determined by thermogravimetry and chemical analysis

Reaction	TiO_2	Weight loss (mg)	Ni content (mg)	Ni(%)		
				TG	Total	Chemical analysis
Reduction of NiO	I	0.46	1.68	6.8	11.2	13
	II	0.29	1.06	4.3		

Sample weight 24.45 mg.

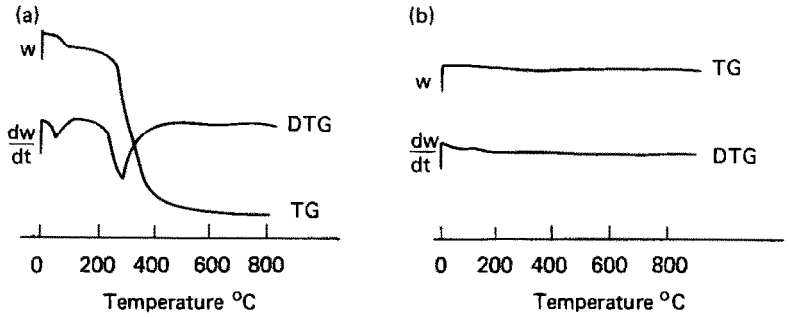

Fig. 7. TG–DTG curves of NiO/glass catalyst reduced by H_2: (a), sample calcined at 400 °C; (b), sample calcined at 900 °C.

Reduction of calcined NiO / Glass under H_2

The TG–DTG curves of NiO/glass (calcined at 400 and 900 °C) reduced in H_2 are shown in Fig. 7, and their XRD patterns are given in Fig. 8.

There are two peaks in the DTG curve of reduced NiO/glass calcined at 400 °C (Fig. 7), and the relevant weight loss is recorded in the corresponding TG curve. The first peak, below 100 °C is the peak of surface water desorption. The second peak in the range 230–335 °C, with a peak temperature of 287 °C, shows the reduction of NiO. The calculated and determined Ni contents are compared in Table 5. Possibly because of the non-homogeneous impregnation of the catalyst, the calculated Ni content is not consistent with the determined value.

The XRD patterns show that, except for the characteristic peak of SiO_2, the remainder is NiO phase, demonstrating that no interaction takes place between NiO and the glass carrier.

There are no peaks or weight loss in the DTG–TG curves of reduced NiO/glass calcined at 900 °C. It is possible that a new compound is formed by the reaction of NiO and glass on calcination at 900 °C and that the new compound cannot be reduced by H_2 in the temperature range from room temperature to 900 °C, otherwise the reduction peak of NiO would appear.

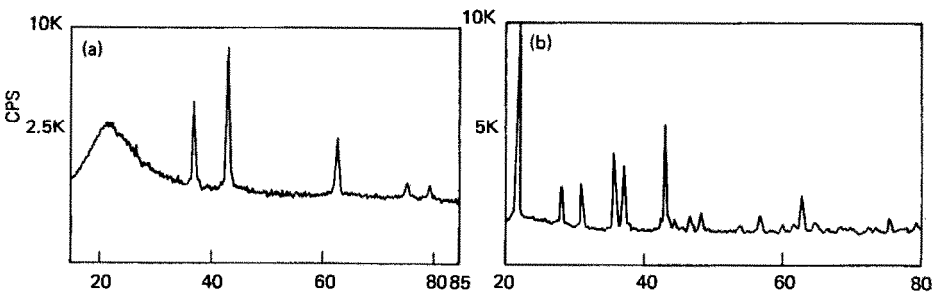

Fig. 8. XRD patterns of NiO/glass catalyst: (a), sample calcined at 400 °C; (b), sample calcined at 900 °C.

TABLE 5

Ni content of NiO/glass determined by thermogravimetry and chemical analysis

Reaction	Weight loss (mg)	Ni content (mg)	Ni (%)	
			TG	Chemical analysis
Reduction of NiO	0.60	2.20	5	3.8

Sample weight 43.45 mg.

The XRD patterns show the diffraction peak of NiO, as well as a definite characteristic peak of a new phase but because of the complicated composition of the glass, its formula is unknown.

CONCLUSION

The effect of calcination temperature on the interaction of active component and support has been studied by thermo-reduction analysis and in situ X-ray diffraction techniques. The experimental results show that the active component NiO interacted with Nb_2O_5 carrier to form $NiNb_2O_6$ when the catalyst was calcined at 400 or 450 °C. No interaction or no distinct interaction of NiO with support was observed with Al_2O_3, TiO_2 or glass. When the catalyst was calcined at 900 °C, there was interaction between NiO and Al_2O_3 or TiO_2 to produce $NiAl_2O_4$ or $NiTiO_3$. Glass also interacted with NiO, but the compound formed has not yet been identified. Combined thermo-reduction analysis and in situ X-ray diffraction techniques have been shown to be an effective method in the elucidation of the interaction of metallic oxide with support.

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