Journal of Thermal Analysis, Vol. 18 (1980) 517–525

THERMOGRAVIMETRY OF THE $NiO-Al_2O_3$ SYSTEM IN A HYDROGEN FLOW

T. N. SOBOLEVA, L. A. RUDNITSKY and A. M. ALEKSEYEV

State Institute for the Nitrogen Industry (GIAP), Moscow, USSR

(Received August 28, 1979)

Thermogravimetry in a hydrogen flow is used to distinguish different forms of $NiO-Al_2O_3$ bonding at the temperatures of reduction of NiO. The influences of the temperature of preliminary treatment and the component ratio on the shapes of the TG and DTG curves of reduction were represented.

By comparison of the results obtained with different weights and with different particle sizes, the influences of diffusion of water vapour in macropores on the characters of TG and DTG curves were studied.

Different types of TG and DTG curves of reduction were observed:

1. Curves usual in thermal analysis, whose positions depend on the specimen weight and on the dispersity of the sample.
2. Curves whose position displays almost no change with variations of 1–2 orders the specimen weight.
3. Curves the number of reduction rate peaks in which depend on the experimental conditions.

Thermogravimetry in a reducing gas flow may, in principle, be used to reveal and distinguish different compounds, including metallic oxides, by means of separating the forms of a bound metal according to its temperatures of reduction.

As is demonstrated below, the correct choice of the experimental conditions is of utmost importance in solving this problem.

The present work deals with the investigation of the possibility of using such a method to study the $NiO-Al_2O_3$ system.

In the course of preparation of nickel – alumina catalysts and in particular during their heat treatment, various compounds of NiO with Al_2O_3 may be formed. The reaction between the active component NiO and the support Al_2O_3 plays an important role, affecting both the nature and conditions of reduction and the properties of the reduced catalyst. However, the investigation of this system encounters some difficulties. For instance, X-ray structure analysis does not always reveal the weak bond of NiO with the support or identify the compounds formed. Various methods [1–4] have been used to study the $NiO-Al_2O_3$ system. For this purpose we have used thermogravimetry in a hydrogen flow, with a linear heating rate.

Experimental

The reduction was carried out on a Sartorius electromicrobalance, which had been adapted for the gas flow and for operation in the temperature range 20 – 1000° [5]. The gas flow was passed through two symmetric tubes. In one of them a quartz dish (12 mm diameter) containing a sample was suspended, while in the other tube there was a similar dish with a counterweight.

The flow rate of the hydrogen (purified by diffusion through palladium) was 20 l/hr. The linear heating rate was 5°/min.

The binary system NiO – γ-Al_2O_3 was investigated at different component ratios. The mixtures were prepared by evaporating a solution containing nickel and aluminium salts, followed by calcination in air at 1000°. In the study of the influence of the dispersity, the binary system NiO – α-Al_2O_3 with the molar ratio 1 : 7 (simulated methane conversion catalyst) was used. This was prepared by impregnating α-Al_2O_3 granules with a solution of a nickel salt, followed by calcination at different temperatures.

The experimental data were represented as TG curves (α vs. T, where α is the degree of reduction, and T is temperature), and as DTG curves $\left(\frac{d\alpha}{dT} \text{ vs. } T\right)$.

Results and discussion

The series of TG and DTG curves illustrating the reduction of the NiO – Al_2O_3 samples with different component ratios are presented in Fig. 1 (the samples were all calcined at 1000° for 3 hours). The curve of the reduction of NiO (curve 1) is also shown in Fig. 1. A comparison of curves 1 and 2 shows that even small additions of Al_2O_3 raise the temperature of reduction of NiO. The increase of the concentration of γ-Al_2O_3 leads to the prevalence of high-temperature forms and the disappearance of low-temperature ones (curves 3 and 4).

A series of TG and DTG curves are shown in Fig. 2 for a methane conversion catalyst, in which NiO is formed on an α-Al_2O_3 support by impregnation. The diagram indicates how NiO progressively forms a strong bond with the support (the formation of a solid solution of Ni – Al spinel in α-Al_2O_3) under the influence of calcination cycles in air at 1000°. The DTG curves in Figs 1 and 2 are sufficiently typical. 1 to 3 peaks of reduction rates can be observed in each of them.

While collating the data obtained in the investigation of NiO – Al_2O_3 systems, we found a considerable number of different reduction rate peaks, with extremely varied values of the temperature maxima. It was necessary to analyze the nature of these peaks and find out whether all of them corresponded to definite, stable forms of bound NiO. To do this, an investigation was carried out on the influence of factors such as the particle size and the variations of specimen weight on the characters of the TG and DTG curves.

Experiments involving the degree of grinding of the granules and considerable variations in the specimen weight (10 to 100 times) were designed to help give information about the extent to which the shapes of TG and DTG curves are determined by the character of the bonding of the $NiO-Al_2O_3$ compound formed during the preparation and how much this shape depends on such "external" factors as the pressure of water vapour (the influence of the specimen weight)

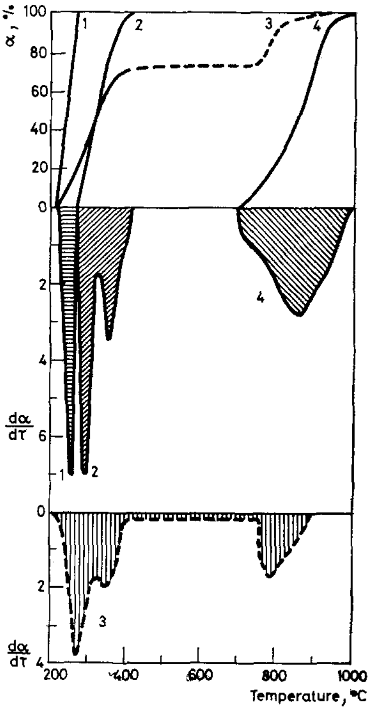

Fig. 1. TG and DTG curves of reduction in a hydrogen flow: 1 — NiO, temperature of preliminary calcination 380°; 2—4 $NiO-\gamma\text{-}Al_2O_3$ mixtures, temperature of preliminary calcination 1000°, molar ratio NiO to $\gamma\text{-}Al_2O_3$; 2 — 7 : 1, 3 — 1 : 1, 4 — 1 : 7; sample weight 0.6 mg NiO

and the diffusion rate of water vapour in the macropores (the influence of the particle size).

The method used to a certain degree allowed separation of the reduction reactions proceeding in the kinetic region, from those the rate of which depends appreciably on the diffusion of water vapour.

The results obtained showed that the DTG peaks and the TG curves of reduction of the $NiO-Al_2O_3$ systems can be divided into several groups. The first group, which is usual for thermal analysis in air or in an inert gas, contains the peaks (or TG curves) the positions of which are changed to some extent by grinding of the granules of sample, or by diminishing the specimen weight.

Examples of such curves are presented in Fig. 3. TG curves 3, 4 and 5 for the reduction of three individual catalyst granules, coincide. However, an identical specimen weight of a powder obtained by grinding of a granule yields, upon

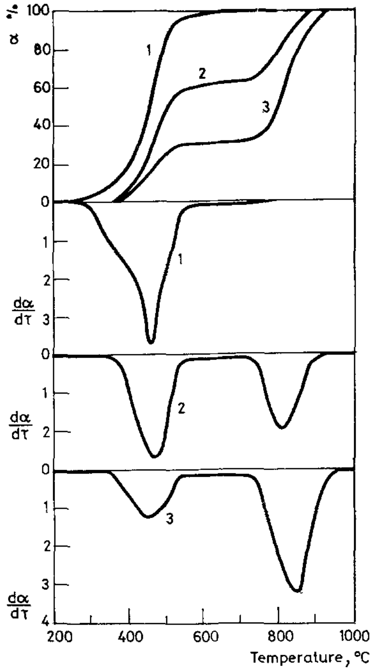

Fig. 2. TG and DTG curves of reduction of NiO—α-Al$_2$O$_3$ with a different number of calcination cycles in air at 1000°: 1 — one, 2 — two, 3 — three cycles; sample weight 60 mg

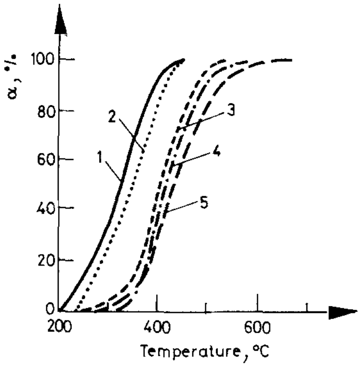

Fig. 3. TG curves of reduction of NiO—α-Al$_2$O$_3$ with molar ratio 1 : 7 temperature of preliminary calcination in air 800°. Specimen weight: 1: 1.2 mg, powder, 2: 9 mg, powder, 3: 9 mg, granule, 4: 9 mg granule, 5: 9 mg granule

reduction, a TG curve (2) shifted by 75° to lower temperature. When the powder weight is decreased 10-fold, the TG curves (1) shifts further to lower temperature (by 25°). These phenomena are explained by the influence of water vapour diminishing the reduction rate. On the change from a low specimen weight to a high one, and from powders to granules, the water vapour pressure increases and the reduction rate diminishes.

In a number of cases the influence of water vapours on the character of the curves proves to be so considerable that the choice of the reduction conditions can affect not only the position, but also the quantity of the DTG peaks of reduction. We attribute such peaks to the second group. Curve 2 in Fig. 4 shows the dependence of the reduction rate of a methane conversion catalyst on the temperature. The curve has 2 peaks, the higher-temperature one seeming to relate to the reduction of a solid solution of Ni—Al spinel in α-Al$_2$O$_3$. The identification of the low-temperature peak is difficult because, as is seen from a comparison of curves 1 and 2, on grinding of the granules this peak is divided into two. One of them, B′, corresponds to the peak B displaced as a result of grinding the granules (this displacement is about the same as that in Fig. 3). The other peak, A′, is in the region of NiO reduction.

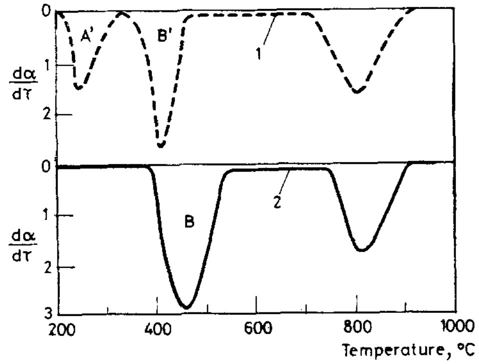

Fig. 4. DTG curves of reduction of NiO—α-Al$_2$O$_3$ with molar ratio 1 : 7, temperature of calcination in air 1000°. Specimen weight: 1: 100 mg, powder, 2: 100 mg, granules

A similar effect was observed in the investigation of the reduction of NiO—γ-Al$_2$O$_3$ powder having a NiO to γ-Al$_2$O$_3$ ratio of 7 : 1 (Fig. 5). On a 50-fold diminishing of the specimen weight, the position of one peak remains the same (290°), whereas the second, higher-temperature peak is displaced to the left. However, the most important fact is that the ratios of the peak areas are changed as a result of the intensity of the higher-temperature peak decreasing in favour of the lower-temperature one. We observed such a regularity for all specimen weights of this sample (from 0.4 to 20 mg). For 20 mg the intensity of the higher-temperature peak is 1.35 times that of the lower-temperature one. For 0.4 mg this ratio is 0.47.

The appearance and disappearance of peaks, as well as the change of the intensity ratio between peaks as a result of changes in the dispersity and the specimen weight of a sample, in our opinion indicate that the water vapour formed during the reduction plays an active part. When the conditions of an experiment (a high specimen weight or a coarse granule) favour the increase of the concentration of water vapour up to some "critical" value, the water vapour catalyzes the interaction between weakly-bound NiO and Al_2O_3. As a result, a higher-temperature form of NiO$-Al_2O_3$ is formed, i.e. a new peak appears.

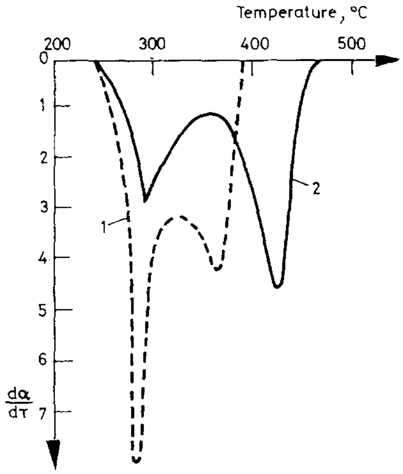

Fig. 5. DTG curves of NiO$-\gamma$-Al_2O_3 with molar ratio 7 : 1, temperature of calcination 1000°. Specimen weight: 1: 0.4 mg, 2: 20 mg, powder

In some cases even, Ni$-$Al spinel is formed under the influence of the water vapour formed in the course of reduction. Figure 6 shows the DTG curves of reduction of a NiO$-\gamma$-Al_2O_3 sample calcined at 1000° for 3 hours (NiO : Al_2O_3 = = 1 : 1). Curve 1 refers to a powder specimen 1.6 mg. The high-temperature peak conforms to the reduction of the Ni$-$Al spinel obtained during the calcination. The intensity ratio of the low-temperature peaks A : B is 2.1. The ratio of the intensity sum of the low-temperature peaks A + B to the intensity of the high-temperature one C is 2.3.

In conformity with the above results, on increase of the specimen weight up to 22 mg the intensity ratio of the low-temperature peaks becomes $A' : B' = 0.6$ (curve 2). What is more, the ratio between the intensity sum of the low-temperature peaks and the intensity of the spinel peak $(A' + B') : C'$ is already 1.1. This indicates the increase of the spinel concentration.

At the same time, the position of the high-temperature peak of spinel reduction is almost insensitive to the specimen weight. This peak belongs to the third group of TG or DTG curves, whose position is practically independent of the specimen weight, and in some cases also the sample dispersity (this latter concerns only the high-temperature TG curves). These are the curves of reduction of NiO (Fig. 7, curves 1, 2, 3), for which a 100-fold change in the specimen weight causes a temperature shift of no more than 10°, and also the curves of reduction of a solid solution of Ni—Al spinel in α-Al$_2$O$_3$, for which the curves obtained on the reduction of granules (curve 6) coincide well with the curves obtained on the reduction of powder (curves 4 and 5).

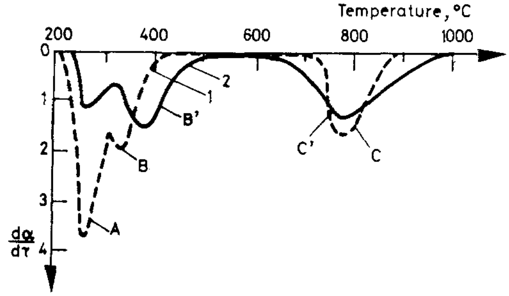

Fig. 6. DTG curves of reduction of NiO—γ-Al$_2$O$_3$ with molar ratio 1 : 1, temperature of calcination 1000°. Specimen weight: 1: 2.6 mg, 2: 22 mg, powder

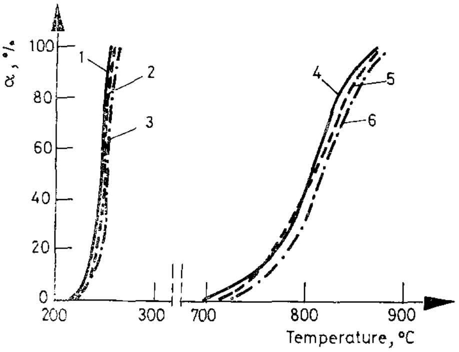

Fig. 7. TG curves of reduction of 1—3 NiO powders calcined in air at 380°. Specimen weight: 1: 0.06 mg, 2: 0.6 mg, 3: 5 mg. 4—6 NiO—α-Al$_2$O$_3$ with molar ratio 1 : 7, temperature of calcination in air 1000°. Specimen weight 4: 10 mg, powder, 5: 3.6 mg, powder 6: 10 mg, granule

The process of reduction of these compounds takes place mainly in the kinetic region, i.e. it is not hindered by diffusion phenomena in a gas phase. Of course, it is achieved by keeping a number of experimental conditions:

1. A sufficiently large space velocity of highly-pure hydrogen.
2. A sufficiently small sample weight.

Thus, there are three groups of DTG peaks (TG curves) relating to reduction of $NiO-Al_2O_3$ systems with hydrogen:

1. the reduction process proceeds mainly in a kinetic region and is weakly hindered by diffusion of water vapour in the gas phase;
2. the reduction process is hindered by the delayed withdrawal of the water vapour formed in the course of reduction;
3. the water vapour catalyzed the formation of stable $NiO-Al_2O_3$ compounds (having a higher temperature of reduction). Of course, in this case the curve shape may not indicate the character of the $NiO-Al_2O_3$ bonds in the system under study.

It seems logical that group 3 does not contain the curves of reduction of NiO (no Al_2O_3) and the curves of reduction of Ni–Al spinel or of a solid solution of Ni–Al spinel in Al_2O_3 (the formation of stable compounds has come to an end at the sample preparation stage).

Since the intensity of the peaks with a changeable maximum position reduced with decreasing specimen weight, analysis by this method is best carried out on the smallest specimen of the powder.

In conclusion, let us consider briefly the question of the stability of the position of a TG curve (DTG peak) which corresponds to the studied compounds (NiO, Ni–Al spinel, etc).

The experimental data show that the positions of the curves depend to some extent on the prehistory of the compound (the temperature and medium of the thermal treatment of the sample and of the initial reagents). However, the magnitude of a shift is relatively small. For example, in the formation of NiO the change of the temperature of calcination of the nickel salt from 400 to 900° causes a shift in the TG curve of 30–35°. The change from 1000 to 1400° in the temperature of formation of a solid solution of Ni–Al spinel in α-Al_2O_3 lends to a shift in the TG curve of about 100°.

Accordingly from the position of TG curves of reduction one may sometimes also judge the temperature of formation of a sample of some compound of nickel oxide with the support.

References

1. V. A. Dzisko, S. R. Noskova, M. S. Borisova, L. G. Karakchiev, V. D. Bolgova and T. J. Tulikova, Kinet. Katal., 3 (1972) 366.
2. A. M. Rubinshtein, A. A. Slinkin and N. A. Pribytkova, Izv. Acad. Nauk SSSR, Ser. Khim., (1958) 814.
3. L. K. Freidlin, N. V. Borunova and V. D. Krylov, J. Phys. Chem., 35 (1961) 2458.
4. L. G. Simonova, V. A. Dzisko, M. S. Borisova, L. G. Karakchiev and I. P. Olenkova, Kinet. Katal., 14 (1973) 1566.
5. O. V. Zamjatina, L. A. Rudnitsky, B. D. Agranat, A. M. Alekseev and S. Kh. Egeubaev, Trudy GIAP, 43 (1977) 18.

Résumé — La thermogravimétrie sous courant d'hydrogène a été utilisée afin d'étudier l'influence de la température de réduction de NiO sur les différentes formes de la liaison NiO-Al_2O_3. On a étudié l'influence de la température du traitement préliminaire et celle du rapport des composants sur l'allure des courbes TG et TGD lors de la réduction.

En comparant les résultats obtenus avec des prélèvements de poids différents et des dimensions différentes de particules, on a étudié l'influence de la diffusion de la vapeur d'eau dans les macropores sur l'allure des courbes TG et TGD.

On a observé différents types de courbes TG et TGD lors de la réduction:

1. des courbes, habituelles en analyse thermique, dont la position dépend du poids et de la dispersion du prélèvement;
2. des courbes dont la position ne varie presque pas avec des variations du poids du prélèvement de 1 à 2 ordres de grandeur;
3. des courbes dont le nombre de pics de vitesses de réduction dépend des conditions d'expériences.

Zusammenfassung — Es wird die thermogravimetrische Analyse im Wasserstoffstrom zur Differenzierung der verschiedenen Formen der NiO-Al_2O_3-Bindungen je nach der Reduktionstemperatur von NiO angewendet. Der Einfluß der Temperatur der Wärmevorbehandlung und des Verhältnisses der Komponenten NiO und Al_2O_3 auf die Gestalt der TG- und DTG-Reduktionskurven wurde untersucht.

Durch Vergleich der mit verschiedenen Probeeinwaagen und verschiedenen Teilchengrößen erhaltenen Ergebnisse wurde der Einfluß der Wasserdampdiffusion in Makroporen auf den Charakter der TG- und DTG-Kurven untersucht.

Verschiedene Typen der TG- und DTG-Reduktionskurven wurden beobachtet:

1. Kurven, üblich für die Thermoanalyse, deren Lage von der Einwaage und von der Dispersität der Probe abhängig ist.
2. Kurven, deren Lage sich bei Änderungen der Einwaage um 1—2 Größenordnungen nahezu nicht verändert.
3. Kurven, bei denen die Zahl der Reduktionsgeschwindigkeitsspitzen von den Versuchsbedingungen abhängig ist.

Резюме — Рассматривается возможность применения термогравиметрии в токе водорода для дифференциации различных форм связи NiO—Al_2O_3 по температурам восстановления NiO. Приведены результаты исследования влияния температуры предварительной термообработки и соотношения компонентов на форму кривых TG и DTG восстановления.

Путем сопоставления результатов, полученных на навесках порошков различной величины и гранулах, исследовали влияние диффузии водяного пара в макропорах на характер кривых TG и DTG.

Наблюдали различные типы кривых TG и DTG восстановления:

1. Кривые, обычные для термоанализа, положение которых зависит от навески и дисперсности образца.
2. Кривые, положение которых почти не изменяется при вариациях навески на 1—2 порядка.
3. Кривые с зависящим от условий эксперимента числом пиков скоростей восстановления.