

THERMAL BEHAVIOUR OF HIGH SURFACE AREA V₂O₅/TiO₂ CATALYSTS

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Thermal analysis (TG and DTA) was employed for the characterization of V₂O₅/TiO₂ catalysts supported on high surface area TiO₂. The results obtained are consistent with a uniform spreading of vanadium oxide on TiO₂ surface for V₂O₅ content less than 15% by weight.

The presence of V₂O₅ on the surface of TiO₂ affects the anatase-rutile phase transition lowering the temperature at which it occurs.

DTA measurements, performed on catalysts after many months from the preparation, show the appearance of an exothermic peak in the range 280°–340°C. This signal has been related to the oxidation of V(IV) to V(V) on the catalyst surface.

Catalysts characterization, performed by chemical analysis and FT-IR spectroscopy, has confirmed this interpretation.

It has been suggested that a slow modification of the catalyst occurs, leading to an increase of the V(IV) content during the time.

Keywords: high surface area, V₂O₅/TiO₂ catalysts

Introduction

V₂O₅/TiO₂ systems are the most effective catalysts for selective catalytic reduction (S.C.R.) of nitrogen oxides with ammonia [1]. The best performances are obtained with catalysts having a V₂O₅ content not exceeding monolayer coverage [2].

Recent studies have shown that the interaction between V₂O₅ and TiO₂ leads to the formation of vanadium oxide species having specific catalytic properties towards NO reduction [3–5].

The nature of vanadium oxide species constituting the monolayer has been investigated by different techniques [4–7]. However thermal analysis was scarcely employed to characterize the V_2O_5/TiO_2 systems [8, 9].

In a recent work [10] we have studied chemical and physical properties of high surface area V_2O_5/TiO_2 catalysts prepared by supporting V_2O_5 on laser synthesized ultrafine TiO_2 powders. In this work we have employed the DTA and TG techniques in order to study the thermal stability of V_2O_5/TiO_2 catalysts. Moreover, by such techniques, a further contribution to the characterization of vanadium oxide species formed on the catalyst surface has been achieved.

Experimental

The V_2O_5/TiO_2 catalysts were obtained by impregnation with NH_4VO_3 solution of high surface area ($128\text{ m}^2/\text{g}$) TiO_2 powder. The TiO_2 support was synthesized by laser pyrolysis technique, as described in [11]. The catalysts were dried in oven at 120°C and then calcined at 400°C in air flow (99.95% purity) for 3 h. The catalysts contained V_2O_5 nominal contents of 4, 8 and 15 wt%.

The chemical analysis of V(IV) and V(V) was effected dissolving the catalysts in concentrated H_2SO_4 and titrating with $KMnO_4$ to determine V(IV) content. The vanadium was reduced to +4 oxidation state with $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ and then titrated with $KMnO_4$ again to determine the total vanadium content.

Thermal analysis was effected by using a DuPont 9000 system constituted by TG and DTA independent units. Both TG and DTA measurements were effected with heating rate of $20\text{ deg}/\text{min}$. The reference for DTA measurements was TiO_2 calcined at 1000°C , which did not show any thermal effect in the whole range of temperature investigated.

IR measurements were effected on a IFS 66 Bruker FT-IR apparatus using the KBr pellets technique.

Results and discussion

The results were obtained on samples as synthesized and after different times from the synthesis.

The results of chemical analysis of catalysts are reported in Table 1 as total vanadium and V(IV) content.

The TG curves for pure TiO_2 and for the catalysts after 1.5 years from the synthesis are shown in Fig. 1. It can be observed a large weight loss for all samples that starts at room temperature and is completed at $300^\circ\text{--}400^\circ\text{C}$. In V_2O_5/TiO_2 catalysts the weight loss decreases with the vanadium content. This weight loss is related to the removal of hydration water and OH surface groups of TiO_2 .

Morishige [12] reported that TiO_2 as anatase phase undergoes removal of most OH surface groups in a temperature range extending up to 400°C . The decreasing of weight loss with vanadium content can be explained by supposing that the surface OH groups of TiO_2 are involved in the interaction with vanadium species, as suggested by Baiker [13]. A further weight loss, absent for pure TiO_2 , is observed at temperature between 650° and 700°C in TG curves of all $\text{V}_2\text{O}_5/\text{TiO}_2$ catalysts. This weight loss starts at lower temperatures and increases by increasing the V_2O_5 content.

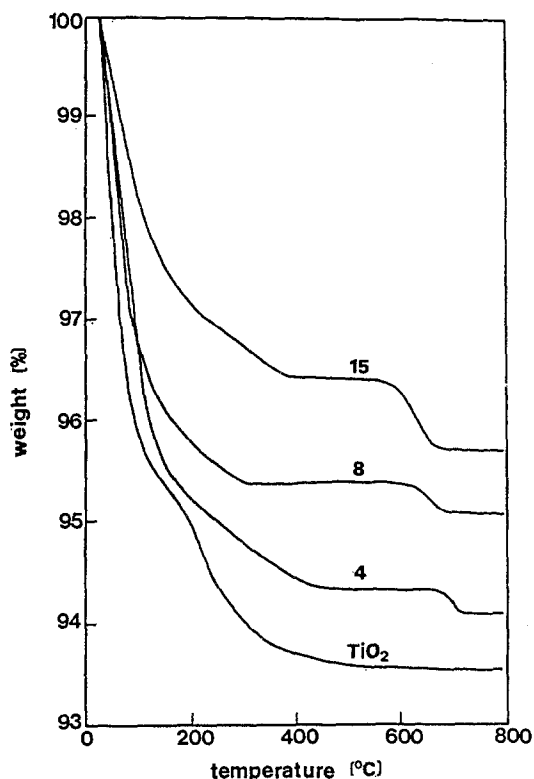


Fig. 1 TG curves of TiO_2 and $\text{V}_2\text{O}_5/\text{TiO}_2$ catalysts (V_2O_5 nominal percentage is reported on the curves)

It was found that in $\text{V}_2\text{O}_5/\text{TiO}_2$ systems the anatase-rutile transition leads to the reduction of V(V) to V(IV), which becomes incorporated in TiO_2 , forming $\text{V}_x\text{Ti}_{1-x}\text{O}_2$ solid solution [9]. The reduction of vanadium oxide involves oxygen evolution detected by TG analysis as a weight loss, which increases by increasing the vanadium content, due to the higher amounts of V(V) (Table 1).

Table 1 Chemical analysis of V_2O_5/TiO_2 catalyst. a) as synthesized b) 1.5 years after synthesis

Nominal V_2O_5 content / wt%	Total V content / wt%	Vanadium(IV) as a fraction of total V content	
		a	b
4	2.2	0.28	0.98
8	4.3	0.23	0.84
15	7.8	0.13	0.30

The DTA curves obtained on pure TiO_2 and on the catalysts, as synthesized and after 1.5 years from the synthesis, are shown in Figs 2 and 3 respectively.

DTA curves of all the samples show endothermic peaks with maxima ranging from 100° to $150^\circ C$. The intensity is higher for the samples of Fig. 3. These

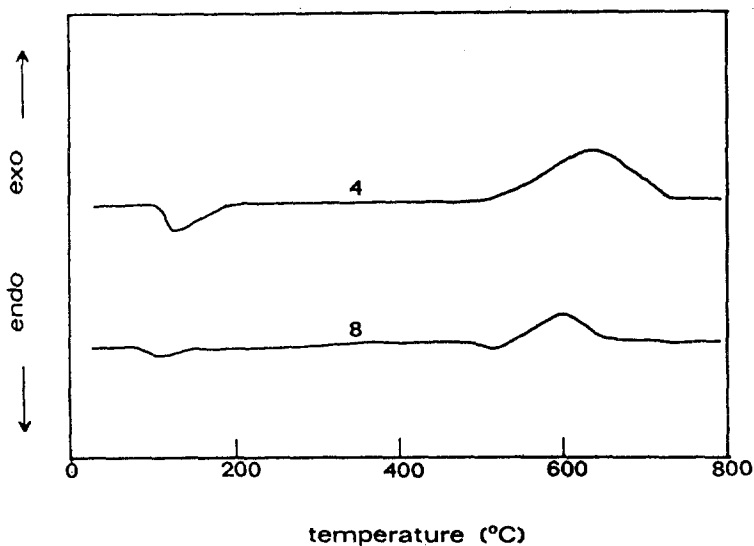


Fig. 2 DTA curves of TiO_2 and V_2O_5/TiO_2 catalysts as synthesized (V_2O_5 nominal percentage is reported on the curves)

peaks, which correspond to a large weight loss in TG curves, can be related to dehydration of the samples.

DTA curve of pure TiO_2 shows an exothermic peak at about $760^\circ C$ which can be attributed to anatase-rutile transition [14]. On DTA curves of V_2O_5/TiO_2 samples we can note exothermic peaks with maxima between 560° and $600^\circ C$ which shift to lower temperature by increasing vanadium content. These signals are also related to TiO_2 transition from anatase to rutile phase. It was reported

[9, 14] that the temperature at which this transition occurs is lowered by the presence of impurities or metal oxides dispersed on TiO_2 surface, the promoting effect of V_2O_5 on anatase-rutile transition being related to the formation of a solid solution between TiO_2 rutile and VO_2 . It must be remarked that, even at V_2O_5 content close to monolayer completion, the temperatures of anatase-rutile transition are higher than those of interest for S.C.R. process [1].

In the catalyst containing 15 wt% V_2O_5 a sharp endothermic peak at 670°C is present which is associated to melting of crystalline V_2O_5 . In [10] we have studied $\text{V}_2\text{O}_5/\text{TiO}_2$ catalysts obtained by impregnation of the same support. We have found that a monolayer oxide is completed at about 12–13 wt% V_2O_5 . The DTA measurements show, in agreement with the above results, that a segregated V_2O_5 phase is present only in the catalysts with V_2O_5 content higher than monolayer coverage.

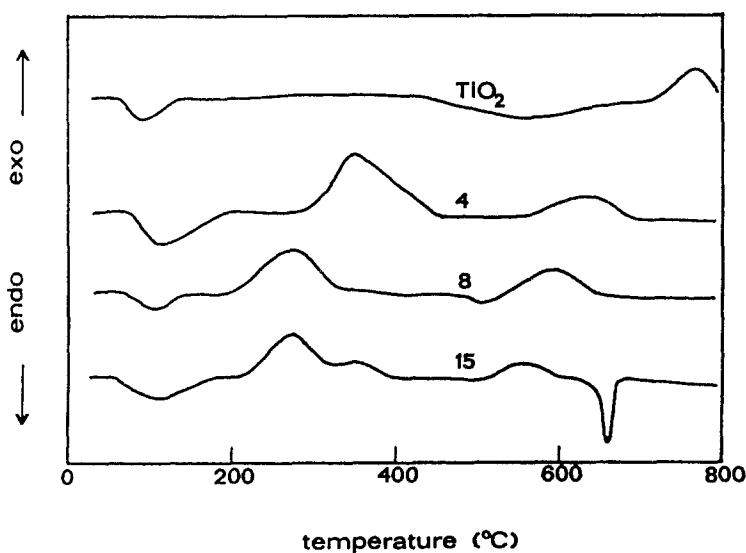


Fig. 3 DTA curves of TiO_2 and $\text{V}_2\text{O}_5/\text{TiO}_2$ catalysts 1.5 years after the synthesis (V_2O_5 nominal percentage is reported on the curves)

Exothermic peaks with maxima at $280^\circ\text{--}340^\circ\text{C}$ appear on DTA curves of catalysts after 1.5 years from the synthesis (Fig. 3), but not on DTA of catalysts as synthesized (Fig. 2). We have associated these signals to the oxidation of V(IV) containing oxide species on the base of the following observations:

a) chemical analysis of V(IV) and V(V), performed on the samples taken from DTA apparatus after heating at 400°C , shows that the percentage of V(IV) is reduced as effect of thermal treatment, becoming comparable to the V(IV) content of the catalysts as synthesized;

b) exothermic peaks are no longer observed performing DTA measurements on samples heated at 400°C.

These results indicate that the content of V(IV) in the catalysts was slowly increasing with the time. The reduction of V(V) is a reversible process, V(IV) being easily reoxidized by thermal treatment in air.

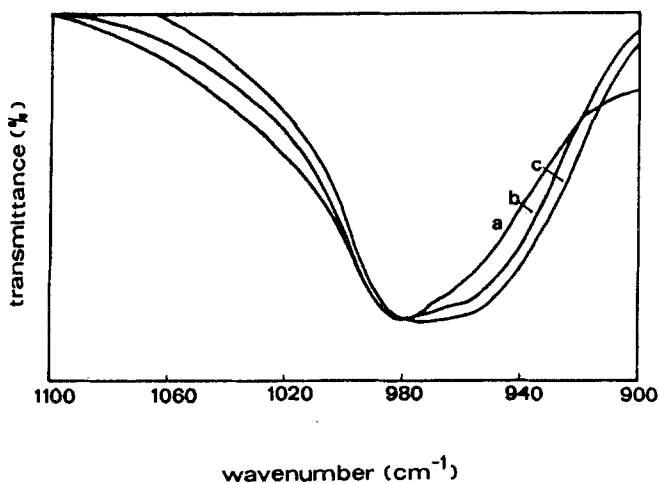


Fig. 4 IR spectra of catalysts containing 4 wt% V₂O₅: a) as synthesized, b) 15 days and c) 6 months after the synthesis

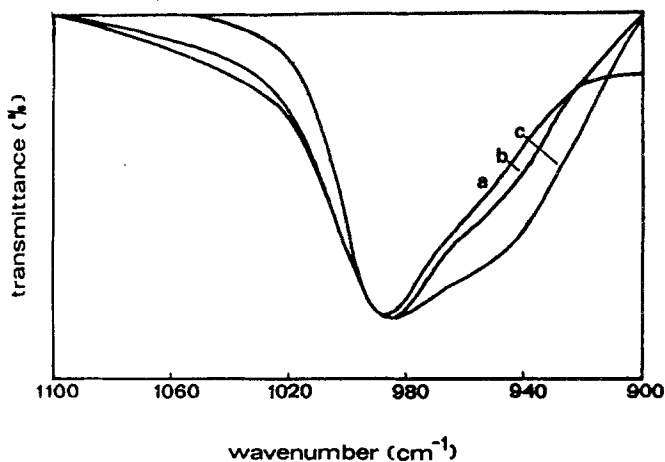


Fig. 5 IR spectra of catalysts containing 8 wt% V₂O₅: a) as synthesized, b) 15 days and c) 6 months after the synthesis

In order to ascertain this effect we have performed IR measurements at different time from the synthesis on catalysts containing 4 and 8 wt% V₂O₅. In Figs 4 and 5 IR spectra obtained on samples as synthesized, after 15 days and 6 months from the synthesis are reported. We can note that the IR spectra of both the catalysts show signals at 980 and 940 cm⁻¹ and this latter increases with time.

As reported in [10] the signal at 980 cm⁻¹ can be attributed to a V(V) oxide species and that at 940 cm⁻¹ to a V(IV) species. Therefore these results confirm the slow modification of the catalyst that involves an increase of V(IV) amount. It must be remarked that the IR spectra appear somewhat different from those reported in [10], which displayed a higher intensity ratio of 940 to 980 cm⁻¹ signals. This is probably due to the different modality of calcination, which in [10] was performed in static air. The consequent higher concentration of water and ammonia in the calcination atmosphere, in respect to flow condition, could promote the V(IV) formation, as suggested in [15].

It is worth noting, that in the fresh catalysts, a fraction of vanadium, corresponding to about 1 wt%, is in +4 oxidation state. This amount is scarcely dependent on the total vanadium content. Therefore the corresponding V(IV) containing oxide species seem to be related to a specific interaction between active phase and support. This vanadium fraction pertains in +4 oxidation state even after heating at 400°C in air. The presence, within the monolayer, of vanadium species having different stability towards oxidation could affect the catalytic properties of V₂O₅/TiO₂ systems.

References

- 1 H. Bosch and F. Janssen, *Catal. Today*, 1 (1988) 369.
- 2 G. C. Bond and S. Flamerz-Tahir, *Appl. Catal.*, 71 (1991) 1.
- 3 W. C. Wong and K. Nobe, *Ind. Eng. Chem. Res.*, 25 (1986) 179.
- 4 J. Haber, A. Kozłowska and R. Kozłowski, *J. Catal.*, 102 (1986) 52.
- 5 G. C. Bond, I. P. Zurita and S. Flamerz, *Appl. Catal.*, 27 (1986) 353.
- 6 G. Ramis, G. Busca, F. Bregani and P. Forzatti, *Catalytic Science and Technology*, Vol. 1, (S. Yoshida, N. Takezawa and T. Ono Eds.), Kodausha, Tokyo 1991, p. 189.
- 7 R. A. Rajadhyakasha, G. Hausinger, H. Zeilinger, A. Ramstetter, H. Schmelz and H. Knozinger, *Appl. Catal.*, 51 (1989) 67.
- 8 R. Y. Saleh, I. E. Wachs, S. S. Chan and C. C. Chersich, *J. Catal.*, 98 (1986) 102.
- 9 G. C. Bond, A. J. Sarkanj and G. A. Parfitt, *J. Catal.*, 57 (1979) 479.
- 10 P. Ciambelli, G. Bagnasco, L. Lisi, M. Turco, G. Chiarello, M. Musci, M. Notaro, D. Robba and P. Ghetti, *Appl. Catal.*, 1 (1992) 61.
- 11 F. Curcio, M. Musci, M. Notaro and G. De Michele, *Appl. Surf. Sci.*, 46 (1990) 225.
- 12 K. Morishige, F. Kamo, S. Ogawara and S. Sasaki, *J. Phys. Chem.*, 89 (1985) 4404.
- 13 A. Baiker, P. Dollenmeier, M. Glinski and A. Reller, *Appl. Catal.*, 35 (1987) 351.
- 14 A. Dassler, A. Feltz, J. Jung, W. Ludwig and E. Kaiserberger, *J. Thermal Anal.*, 33 (1988) 803.
- 15 G. Centi, E. Giamello, D. Pinelli and F. Trifirò, *J. Catal.*, 130 (1991) 220.

Zusammenfassung — Zur Charakterisierung von V_2O_5/TiO_2 -Katalysatoren auf hochoberflächigem TiO_2 Trägermaterial wurde die Thermoanalyse (TG und DTA) angewendet. Für einen V_2O_5 -Gehalt von weniger als 15 Gew.% entsprechen die erhaltenen Ergebnisse einer gleichmäßigen Verteilung des Vanadiumoxides an der TiO_2 -Oberfläche.

Die Gegenwart von V_2O_5 an der Oberfläche von TiO_2 beeinflusst die Anatas-Rutil-Phasenumwandlung, indem sie die zugehörige Temperatur verringert.

DTA-Messungen an Katalysatoren mehrere Monate nach ihrer Herstellung zeigten das Auftreten eines exothermen Peaks im Bereich $280^\circ-340^\circ C$. Dieses Signal wurde der Oxidation von V(IV) zu V(V) an der Katalysatoroberfläche zugeschrieben.

Diese Interpretation konnte durch eine Charakterisierung des Katalysatoren durch chemische Analyse und FT-IR-Spektroskopie bestätigt werden.

Es wurde angedeutet, daß der Katalysator mit der Zeit einer langsamen Modifikation unterliegt, die zu einem Ansteigen des V(IV)-Gehaltes führt.