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NH_3 TPD STUDY AND THERMAL BEHAVIOUR OF VANADIUM-EXCHANGED TITANIUM PHOSPHATES AS CATALYSTS

Reduction of NO with NH_3

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Abstract

The ion exchange technique was employed for the preparation of VO^{2+} modified titanium phosphates as catalysts for the selective reduction of NO with NH_3. The samples were prepared by contacting with a vanadyl sulphate solution different precursor materials, amorphous, crystalline or sodium half exchanged titanium phosphate. The vanadium contents of modified phosphates were in the range 0.08–2.3 wt%. XRD and thermal analysis TG/DTA showed that vanadium loading does not cause structural modification in hydrogen titanium phosphate. A vanadyl containing phase was obtained when half sodium titanium phosphate was employed. The NH_3 TPD measurements indicated the presence of a wide distribution of NH_3 adsorbing sites with medium-high strength. Catalytic activity measurements were performed under dilute conditions. It was found that the presence of vanadium even in low amounts strongly promote the catalytic activity.

Keywords: layered metal phosphates, NO reduction, vanadium

Introduction

Most of the catalysts employed in the selective reduction of NO by NH_3 in the presence of O_2 (SCR process)

$$4NO+4NH_3+O_2 \rightarrow 4N_2+6H_2O$$

are based on vanadium oxides as active component supported on TiO_2 [1]. The activity of V^{4+} vanadyl containing species has been hypothesized by some authors [2–4].

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Layered tetravalent bis-monohydrogenphosphates with formula $M(HPO_4)_2 \cdot H_2O$ (M=Zr, Ti, Sn) generally known as acid phosphates having an 'α' structure [5], are widely studied inorganic ion-exchangers [6]. They are able to exchange a very large number of cations and among them transition metal ions [7], coordination compounds [7], etc., acting, in this way, as supports for species very often active in catalysis. Previous investigations had shown that oxocations could be exchanged by layered zirconium phosphate phases [7], in particular a completely characterized pure layered vanadyl compound was obtained from the half sodium form of the α-zirconium acid phosphate, $ZrHNa(PO_4)_2 \cdot 5H_2O$ [8]. Accordingly it has been easy to take the α-titanium phosphate phase, $Ti(HPO_4)_2 \cdot H_2O$ [9], isomorphous with α-zirconium phosphate [5], and other titanium phosphate phases, and use them as supports for the VO^{2+} oxocations, with the double advantage of working with the vanadium species in its 4+ oxidation state, as these ion-exchangers generally have a stabilizing effect on the oxidation number of the exchanged cations. Amorphous and layered crystalline hydrogenphosphate and the half sodium exchanged form of the latter were employed as exchangers for VO^{2+}.

In this paper are described the operating conditions for the preparation of the precursors and the vanadium exchanged compounds. TG/DTA measurements together with XRD analyses are reported that allow to define the thermal behaviour of the various materials and their structural transformations with the temperature. Furthermore, a NH_3–TPD investigation on the vanadium exchanged compounds is presented, that consent to have useful information on their surface interactions.

Experimental

Materials

$TiCl_4$, H_3PO_4 and NaOH were Carlo Erba RPE-ACS (analytical grade) products, $VOSO_4 \cdot 5H_2O$ was Fluka 'purissimum'. All other reagents were of the highest available purity.

Catalysts preparation

The catalysts were prepared starting from three different supports: a) amorphous titanium phosphate $Ti(HPO_4)_{1.7}(OH)_{0.6} \cdot 1.7H_2O$ (am-TiP); b) crystalline layered titanium acid phosphate with 'α' structure, α-$Ti(HPO_4)_2 \cdot H_2O$ (α-TiP) and c) half sodium exchanged α-titanium phosphate α-$TiHNa(PO_4)_2 \cdot 4H_2O$ (TiPHNa).

Am-TiP was prepared by precipitation adding a 0.3 M $TiCl_4$ solution (in HCl 2 M) to H_3PO_4 1.25 M, according to a PO_4/Ti=4 molar ratio [9]. The solid was then filtered, washed with distilled water up to pH=3.35 and dried over P_4O_{10}.

α-TiP was obtained by refluxing am-TiP in H_3PO_4 10 *M* for 100 h, using a molar ratio $PO_4/Ti=40$ [9]. After filtration and washing up to *pH*=4, the solid was stored over P_4O_{10}. TiPHNa was prepared by titrating crystalline α-TiP with a NaOH 0.05 *M* solution up to half the cation exchange capacity of α-TiP (c.e.c.=7.75 meq/g). The material was filtered and washed with distilled water and stored over $BaCl_2$ s.s. ($P/P_o=0.92$) [9].

The preparation of the vanadium-exchanged titanium phosphate phases was performed according to the following procedure: aliquots of vanadyl sulphate solutions $2.5\cdot10^{-3}$ *M* $-2.5\cdot10^{-2}$ *M* were contacted with 1 g of each support. The suspensions were stirred for 4 days at 25°C. The powders were filtered off, washed with distilled water and air dried. The solutions were analyzed for Vo^{2+}, Na^+ (for the TiPHNa-derived materials) and *pH*.

The operating conditions of the various materials and their vanadium content expressed either in moles per mole of titanium phosphate or in wt% with respect to the chemical formulas of the anhydrous materials, are summarized in Table 1. The chemical formulae of the three different vanadium containing compounds are the following: $TiH_{1.62}(VO)_{0.04}(PO_4)_{1.7}(OH)_{0.6}\cdot H_2O$ from am-TiP; α-$TiH_{1.9922}(VO)_{0.0039}(PO_4)_2\cdot H_2O$ from α-TiP and $TiH(VO)_{0.12}Na_{0.76}(PO_4)_2\cdot1.5H_2O$ from TiPHNa. The materials have been synthetically indicated as: am-VTiP; VTiP and VNaTiP respectively.

Chemical analysis and physical characterization

Vanadium uptakes were calculated from the concentration changes of the supernatant solutions before and after ion-exchange. Vanadium was oxidized to V^{5+} and then determined potentiometrically by employing a 0.01 *M* $(NH_4)_2Fe(SO_4)_2$ solution as titrant. In the preparation of sample VTiPNa the sodium released to the solution was determined by atomic absorption method on a Varian Techtron model 1100 spectrophotometer.

Thermal analyses were performed on a Stanton Redcroft TG/DTA model 801 instrument (Pt crucibles Pt-Rh thermocouples, heating rate 8°C min^{-1}) in air flow. X-ray powder diffraction patterns were taken on a Philips diffractometer using Ni-filtered CuK_α radiation.

TPD measurements were carried out at 10°C min^{-1} heating rate, in a flow apparatus with a TCD detector [10] on catalysts pretreated at 600°C in He flow.

The BET surface areas were determined on a Quantachrom-Chembet 3000 instrument.

Catalytic activity measurements

Catalytic activity measurements were carried out in a flow apparatus operating at atmospheric pressure [2]. The experimental conditions were the following:

T=200–400°C, NO and NH_3 concentrations=700 ppm, O_2 concentration=27000 ppm and Ar as balance, space velocity=80000 h^{-1}. The anal- ysis of NO and NO_2 was effected by a continuous chemiluminescence apparatus (Beckmann mod. 955), NH_3 was detected by a continuous IR spectrophotometer (Hartmann & Braun mod. Uras 3G). N_2 and N_2O concentrations were measured by gaschromatographic analysis on a double packed 5A molecular sieve-Porapack Q column.

Results and discussion

Catalysts preparation

It can observed from Table 1 that the higher loading is obtained with α-TiPHNa. This can be easily understood by taking into account the structural characteristics of the three supports. Obviously for am-TiP, the vanadium loading occurs through a VO^{2+}/H^+ ion-exchange process between the VO^{2+} ions of the contact solution and the hydrogen of the surfacial PO_3–OH groups. A similar surfacial exchange process occurs for the layered α-TiP, since the interlayer distance of the material (7.59 Å) is a too small entrance way for the incoming hydrated VO^{2+} ions. As a matter of fact, by assuming a surface OH concentration of 3.9 nm^{-2} for both the hydrogen forms [11] and considering that the BET surface area is 55 m^2 g^{-1} for am-TiP and 10 m^2 g^{-1} for α-TiP, a surface vanadium exchange of 0.825 and 0.165 wt% respectively could be expected. The calculated vanadium loading for am-TiP nicely agrees with the corresponding value reported in the last column of Table 1, while for α-TiP, the vanadium content indicates a partial coverage (~50%) of the external surface. Differently from α-TiP, in the case of TiPHNa the VO^{2+} uptake occurs via a VO^{2+}/Na^+ ion-exchange process and, since the interlayer distance of TiPHNa is of 10.4 Å (about 3 Å larger than that of α-TiP), the exchange also takes place between the layers of the exchanger. This is deduced from the *pH* of the contact solution which remains unchanged (a VO^{2+}/H^+ exchange should have given a *pH* lowering, as it occurs for the two previously mentioned precursors) and by the amount of Na^+ released to the solution, much higher than that which can be expected to be present on the surface of the material, and in perfect agreement with the moles of VO^{2+} taken up. The X-ray pattern of the as prepared VTiPNa

Table 1 Operating conditions for the preparation of the different vanadium-containing materials

Samples	Starting material	Solution concentration/ mol dm^{-3}	Solution volume/ ml g^{-1}	Vanadium content/ mol mol^{-1}	Vanadium content/ wt%
VTiP	α-TiP	2.5 10^{-2}	306	0.0037	0.0784
am-VTiP	am-TiP	2.5 10^{-3}	150	0.040	0.839
VNaTiP	α-TiPHNa	2.5 10^{-3}	540	0.120	2.310

material shows that together with the TiPHNa phase, a small amount of a new layered phase with an interlayer spacing of 9.50 Å (angle 2θ=9.3°) is segregated, probably corresponding to a vanadium titanium phosphate compound of the type α-$TiH(VO)_{0.5}(PO_4)_2{\cdot}nH_2O$, similarly to what occurs with the homologue ZrPHNa that gives, according to a VO^{2+}/Na^+ process, the completely characterized layered compound α-$ZrH(VO)_{0.5}(PO_4)_2{\cdot}2.5H_2O$ (d=9.74 Å) [8].

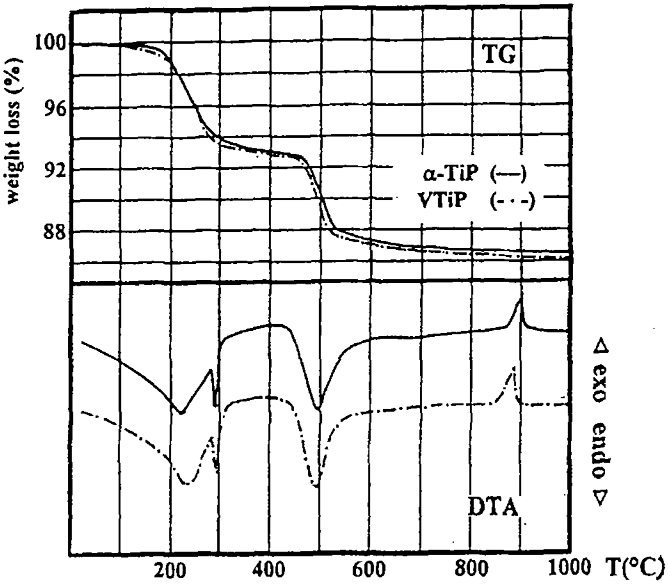

Fig. 1 TG/DTA curves of α-TiP and VTiP

Thermal behaviour and X-ray diffraction analysis

In Figs 1–3 are reported the TG/DTA curves of the three precursor with those of their related vanadium exchanged materials.

No change in thermal behaviour is observed in VTiP sample with respect to α-TiP (Fig. 1). This suggests that the vanadium is mainly present on the surface of α-TiP, in agreement with the ion-exchange data. The TG/DTA curves of VTiP and α-TiP show that the dehydration process corresponding to the loss of 1 mole of water/mole of material, takes place in one step, in the range 40–280°C, with a strong and broad endothermic effect.

The anhydrous phases formed at this temperature undergo, with further heating, a phase transition of which is given evidence in the DTA curves by the sharp endothermic peak with a maximum at about 290°C. In the range 400–600°C, both compounds lose a second mole of water/mole of materials because of the endothermic (see the DTA curves) reaction or condensation of the PO_3–OH groups of the interlayer region to the layered titanium pyrophosphate

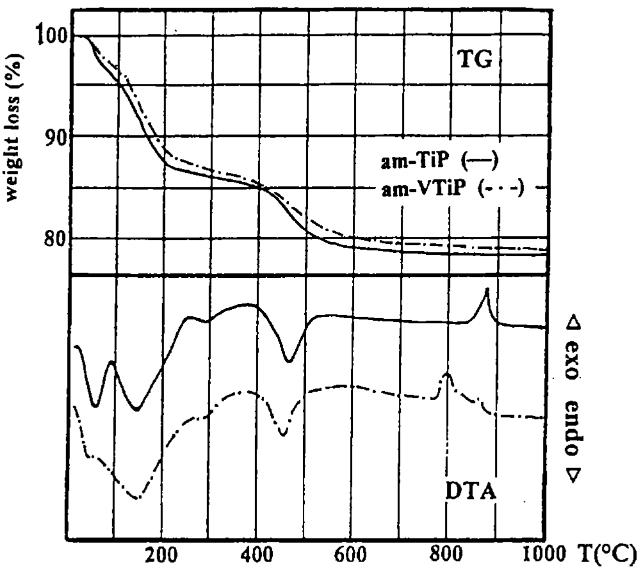

Fig. 2 TG/DTA curves of am-TiP and am-VTiP

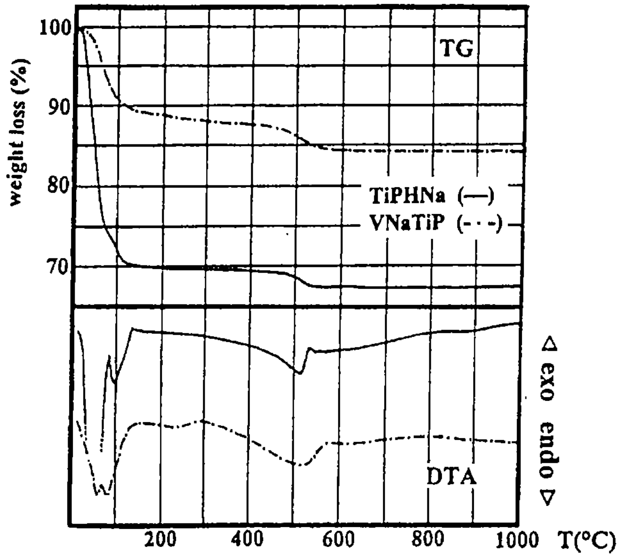

Fig. 3 TG/DTA curves of TiPHNa and VNaTiP

which possesses an interlayer distance of 6.94 Å [12]. The transition to cubic pyrophosphate (α-TiP_2O_7) occurs at about 880°C, and is accompanied by an exothermic peak in the DTA curves. The X-ray diffraction patterns of the two materials taken at the temperature at which the different events occur, are prac-

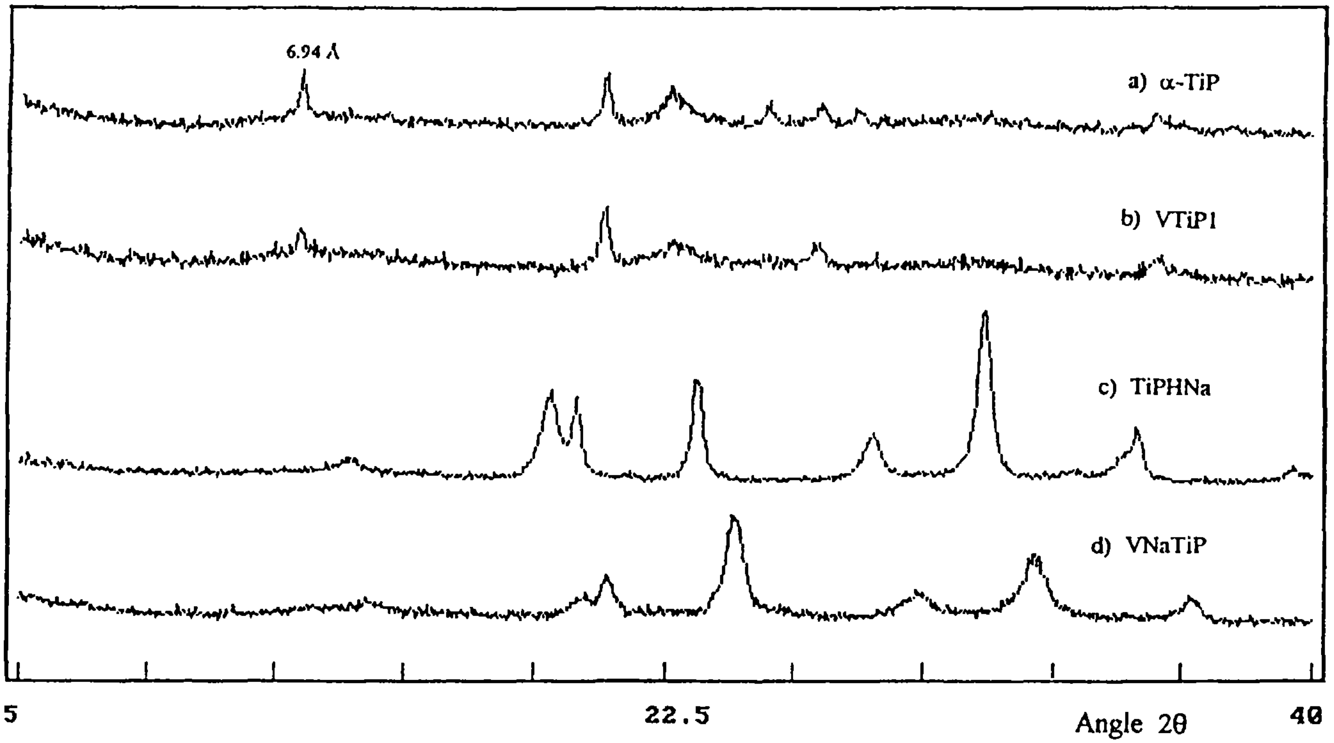

Fig. 4 X-ray diffraction patterns of: a) α-TiP; b) VTiP; c) TiPHNa and d) VNaTiP. All compounds were thermally treated at 600°C

tically superimposable as it can be seen by comparing in Fig. 4 the X-ray spectra of α-TiP and VTiP heated at 600°C, temperature at which the formation of the layered titanium pyrophosphate phase with interlayer distance of 6.94 Å has gone to completion.

The thermal behaviour of the am-VTiP material is very similar to that of the precursor (Fig. 2). For both the dehydration process ends near 300°C and occurs into two steps, differently from α-TiP and VTiP (Fig. 1). It corresponds to a loss of 1.7 moles of water/mole of exchanger. The condensation of the phosphate groups, which also leads to layered titanium pyrophosphates as for the crystalline compounds (the XRD of the materials heated at 600°C are similar to those of Fig. 4a and b), takes place in the range 300–700°C, 200°C wider with respect to α-TiP and VTiP (Fig. 1). The larger temperature interval is to be connected with the structural desorder of the amorphous material. The phase transition to cubic titanium pyrophosphate is also lowered at 850°C.

In Fig. 3 the TG/DTA curves of VNaTiP and precursor TiPHNa are reported. For both the dehydration process occurs in the range 25–350°C, but the weight loss corresponds to four moles of water/mole of TiPHNa (see experimental) and 1.7 moles of water/mole of VTiPNa. The difference is only due to the fact that the precursor has been stored in 92% relative humidity, while the vanadium exchanged compounds has been dried in air. Between 350 and 600°C a condensation process with the loss of 0.5 moles of water/mole of compounds takes place.

The X-ray patterns of TiPHNa treated at 600°C (Fig. 4c) corresponds to that of the tridimensional compound monosodium-dititanium-triphosphate $NaTi_2(PO_4)_3$ [13]. For VNaTiP, the thermal treatment at 600°C leads to a phase which gives an X-ray diffraction pattern (Fig. 4d) with reflexions, if compared with those of the TiPHNa pattern (Fig. 4c), systematically shifted to higher values of angle 2θ, as if the introduction of the vanadium in the structure instead of Na^+ could give rise to a solid solutions.

NH_3 TPD measurements

The results of NH_3 TPD measurements are reported in Fig. 5 and Table 2. The TPD curve of α-TiP shows a broad signal with a maximum at 168°C. This can be related to NH_3 interacting with medium-high strength surface –OH groups of layered pyrophosphates phases [10]. VTiP sample shows a broad signal with maximum at 196°C, more tailed in comparison with the previous one. The amount of NH_3 desorbed (Table 2) is lower than the precursor material. Since only a fraction of the surface –OH is involved in the VO^{2+} exchange, we can suppose that NH_3 is adsorbed either on Brønsted –OH and vanadium species. If we assume that each VO^{2+} adsorbs one NH_3 molecule, it is clear that the amount of NH_3 adsorbed on VTiP is lower than that adsorbed on α-TiP because one VO^{2+} exchanges two H^+ ions. The am-VTiP sample shows a NH_3

curve with higher intensity than that of VTiP, but with the same shape and maximum at 196°C. The amount of adsorbed NH_3, 0.038 mole/mole phosphate, is close to vanadium content, indicating that ammonia is bonded only to vanadium: that is in agreement with the above reported result that all surface hydrogen ions have been exchanged by VO^{2+} ions. Finally TPD curve of VNaTiP sample shows, like as other vanadium containing materials, a broad signal with maximum at 196°C. However the amount of adsorbed NH_3 is lower than am-VTiP sample, not withstanding the higher vanadium content. This result can be explained by the exchange mechanism we have already observed. The vanadium loading occurs via Na^+/VO^{2+} exchange leading both to surface and internal vanadium species. The phase formed after treatment at 600°C retains a high fraction of vanadium in the bulk, which therefore is not accessible to NH_3 adsorption. The NH_3 TPD curve takes into account only the interaction with surface vanadium species.

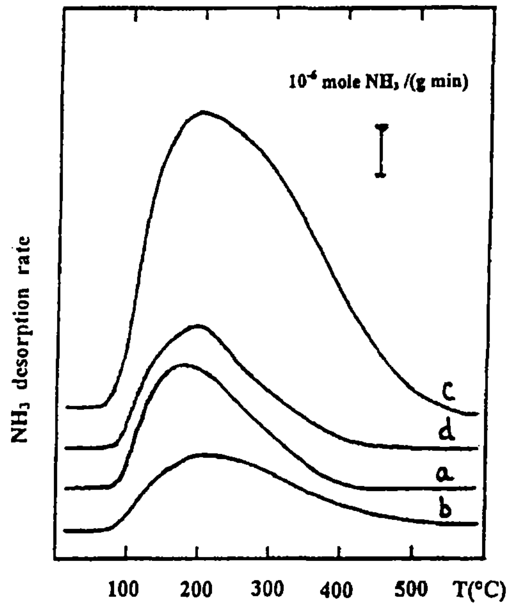

Fig. 5 NH_3 TPD curves: a) α-TiP; b) VTiP; c) am-TiP; d) VNaTiP

Table 2 Results of NH_3 TPD measurements

Sample	Maximum temperature/ °C	Amount of NH_3 adsorbed/ (mole g^{-1})×10^{-5}
α-Tip	168	4.1
VTiP	196	3.5
am-VTiP	196	15
VNaTiP	196	4.2

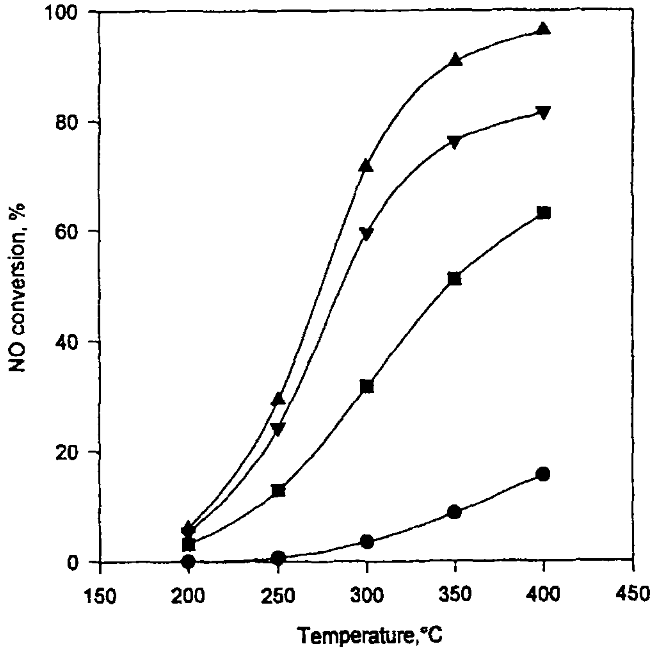

Fig. 6 NO conversion as a function of temperature: (•) α-TiP; (■) VTiP; (▲) am-VTiP; (▼) VNaTiP

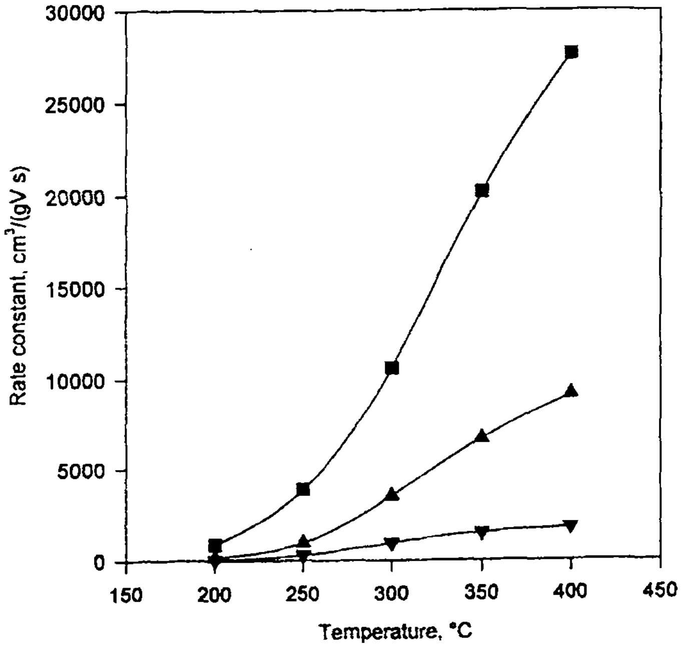

Fig. 7 Rate constant as a function of temperature: (α-TiP; (■) VTIP; (▲) am-VTiP; (▼) VNaTiP

Catalytic activity measurements

Catalytic tests were performed on materials pretreated at 600°C in He flow. In Fig. 6 the NO conversions observed on α-TiP and vanadium modified materials are reported. The activity towards SCR reaction of the parent material is negligible, whatever the temperature. However the presence of vanadium even in low amounts leads to high activity. Moreover NO conversion increases with vanadium content. The vanadium specific constant rates, evaluated on the basis of a first order rate equation (Fig. 7), decreases by increasing the vanadium content, suggesting that different vanadia species are present on the catalyst surface. The above values are higher than those evaluated in [14] for a V_2O_5 supported on pillared titanium phosphate, suggesting a higher activity of vanadyl exchanged titanium phosphates. The results obtained in this work suggest that VO^{2+} present on the surface of titanium phosphates could be the active species in NO reduction with NH_3.

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