Influence of the binder on the properties of catalysts based on titanium–vanadium oxides

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The influence of the nature of the binder and its concentration in V_2O_5/TiO_2 catalysts on their mechanical and catalytic properties has been studied. The characterization analysis showed that the agglomeration mechanism is different when an inorganic acid, such as H_3PO_4, or a natural silicate, such as sepiolite, were used. Two different patterns are proposed, which explain the effect of these binders on the performance of this type of catalyst in the selective catalytic reduction of NO_x with NH_3.

1. Introduction

The V_2O_5/TiO_2 catalytic system has been widely utilized for reactions of partial oxidation of hydrocarbons [1], amoxidation [2] and the selective catalytic reduction (SCR) of NO_x with NH_3 [3] among others. In most of the published papers, in which the behaviour of this type of catalyst is studied, the analyses were usually carried out on powder samples. However, when the objective of the work is to prepare V_2O_5/TiO_2 catalysts for use in industrial reactors, it is necessary to include binding agents in their compostion which will provide suitable mechanical properties.

The inclusion of a binder in this type of catalyst can modify its surface, as well as significantly alter its behaviour. Thus, in a previous study [4], it was shown that H_3PO_4 reacts with the surface of the V_2O_5/TiO_2 catalysts, inhibiting the growth of TiO_2 crystals (anatase) and V_2O_5, giving rise to different titanium and vanadium phosphates, in such a way that their physical and catalytic properties are altered.

In this paper, the effect of H_3PO_4 as a binder is compared with that produced by a natural silicate (sepiolite) added to the catalyst in order to obtain catalysts usable in the industrial decontamination of effluent gases from HNO_3 factories.

There is a possibility of preparing high-activity catalysts by impregnating V_2O_5/TiO_2 on a previously formed support. Nevertheless, it was preferred to prepare catalysts in which the active phase is evenly distributed throughout the mass of the catalyst with the object of prolonging its life, given that the catalysts will be subjected to relatively significant erosion conditions.

2. Experimental procedure

The catalysts used in this study were prepared by impregnating an aqueous solution of ammonium metavanadate (Merck) in a hydrated titanium oxide gel (CLDD 1727. Tioxide) and by concentrating the suspension by evaporation until the percentage of water in the paste is adequate. (When phosphoric acid is used, the paste is dried out and the powder is sieved (diameter ≤ 0.25 mm), then it is mixed with an aqueous dissolution of phosphoric acid, until the mass has a viscosity of about 500000 cP. When sepiolite is used, the paste is concentrated until its content in water is approximately equal to the weight of sepiolite which is added for its extrusion.) The mass obtained was then extruded into 2 mm diameter cylinders which were dried for 12 h in an oven at 110 °C and treated in an air atmosphere at 500 °C for 4 h.

The composition of the catalysts was determined by X-ray fluorescence (XRF), using an SRS 300 sequential spectrometer with a PDP 11/23 evaluation computer. The surface area values were measured by nitrogen adsorption using the BET method in a Micromeritics 2100 D and the pore-size distribution by mercury-intrusion in a Micromeritics 9300 porosimeter.

The measurements of the crushing strength (CS) were carried out in a Chatillon dynamometer and the overall appearance of the surface, as well as the average size of the particles, was determined in a scanning electronic microscope (SEM) ISI DS-130. For the study of the association of V_2O_5 and TiO_2, the SEM was equipped with a Si/Li detector and a Kevex 8000 II processor for energy dispersive X-ray analysis (EDX).

The measurements of catalytic activity were carried out in a fixed-bed tubular reactor, working under piston flow and pseudo-adiabatic conditions.

The analyses of NO and NO_2 at the inlet and outlet of the reactor were carried out by chemiluminescence in a Luminox 201 B (BOC) and the NH_3 and N_2O concentrations were measured by infrared spectroscopy in a Miran 1A (Foxboro).

Two series of catalysts were prepared, the first denoted Series P, was composed of catalysts in which, a constant atomic ratio of Ti/V = 9 was maintained while the concentration of the H_3PO_4 was varied in the range 0–14M. In this way, the phosphorus content present in each of the catalysts ranged between 0 % and 22 % by weight, equivalent to 0 % and 50 % when expressed as P_2O_5. In the second series of catalysts, denoted Series S, the Ti/V = 9 ratio remained constant in all the catalysts but the proportion of sepiolite was varied between 0 % and 100 % by weight.

3. Results and discussion

3.1. SEM–EDX study

Fig. 1a is a scanning electron micrograph corresponding to a catalyst based in Ti–V oxides extruded without any binder. It can be seen that the catalyst is made of pseudo-spherical particles with sizes ranging from 0.05–0.1 μm, which can be found grouped together to form units of varying sizes (0.3–1 μm), in which the original particles maintain their identity. The catalysts with a moderate concentration of P_2O_5, Fig. 1b, show a general appearance similar to the oxide catalysts of titanium and vanadium without binder. However, in the enlarged section of the photograph it can be seen that the agglomerates are more compact, and within them, the particles appear to be stuck together.

The morphology of sepiolite extruded with water and treated at 500 °C can be seen in Fig. 2a. It is made up of particles with sizes ranging from 100–250 μm. These particles are, in turn, composed of bunches of fibres, each having a size that can range from 0.2–1 μm in length and 10–100 nm in width; these observations are in agreement with the structure described by Alvarez et al. [5]. In the catalysts with a sepiolite content higher than 30 wt %, Fig. 2b, it can be seen that the catalyst is composed of sepiolite particles, among whose fibres are dispersed the particles of TiO_2 which are impregnated with the vanadium salt.

Fig. 3 shows the distribution of titanium, vanadium and silicon, through EDX line profiles obtained with their characteristic K_α emissions, respectively. It appears that titanium and vanadium are associated and that silicon is abundant where titanium and vanadium are lacking. These features indicate that vanadium salt has been impregnated on the TiO_2 particles which are dispersed between the sepiolite fibres.

3.2. Mechanical and textural properties

The hardening effect of the binder was determined by measuring the strength necessary to crush 5 mm long cylinders of the catalysts. In Figs 4 and 5, the average crushing strength and the surface area have been plotted versus binder concentration. In general, it can be seen that as the concentration of the binder increases, there is a progressive increase in the crushing strength of the catalyst; this effect is greater for the H_3PO_4 than the sepiolite. However, while H_3PO_4 causes a continuous decrease of surface area, the addition of sepiolite to the V_2O_5/TiO_2 system
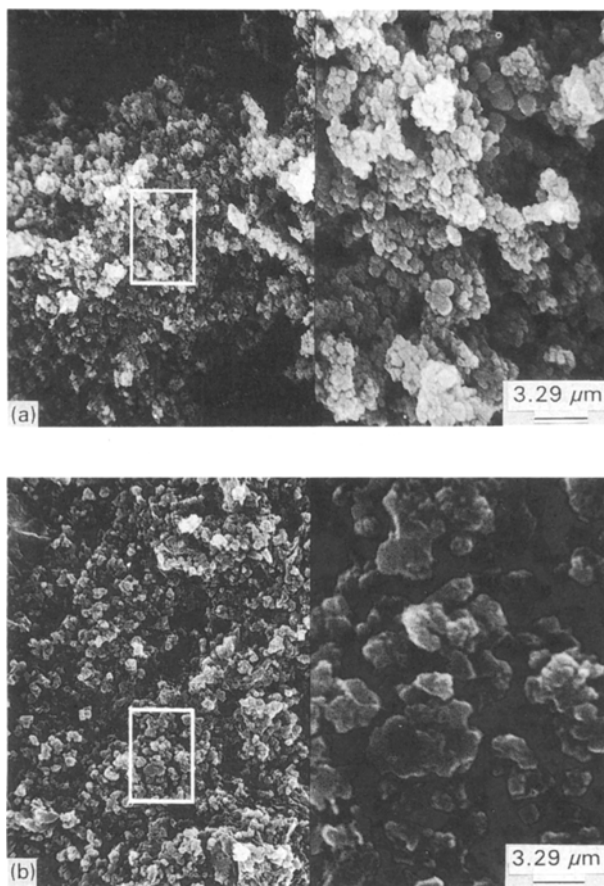

Figure 1 Scanning electron micrographs of (a) TiO_2–V_2O_5 catalyst without any binder, (b) TiO_2–V_2O_5 catalyst with P_2O_5 (28.2 wt %).

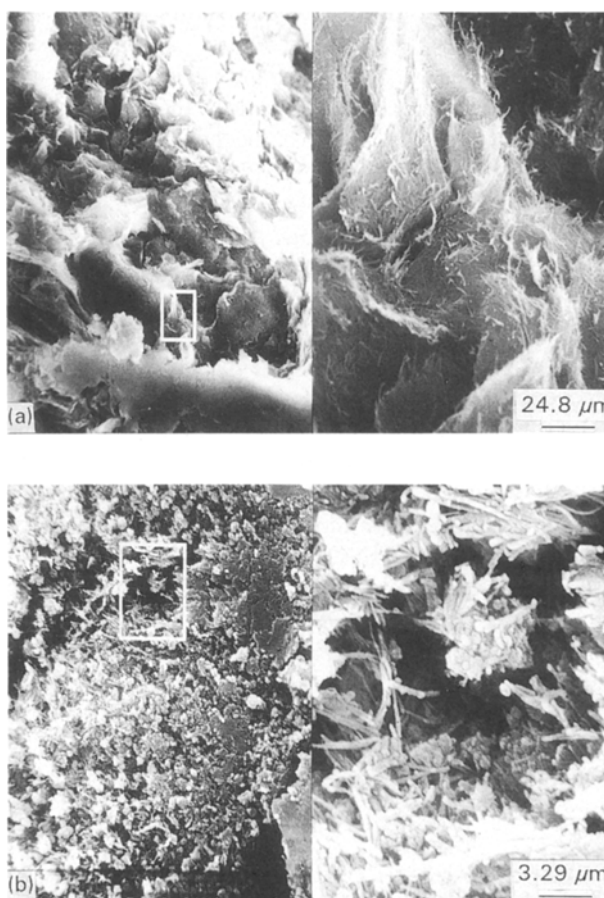
Figure 2 Scanning electron micrographs of (a) sepiolite treated at 500 °C and (b) TiO_2–V_2O_5 catalyst with sepiolite (56.5 wt %).
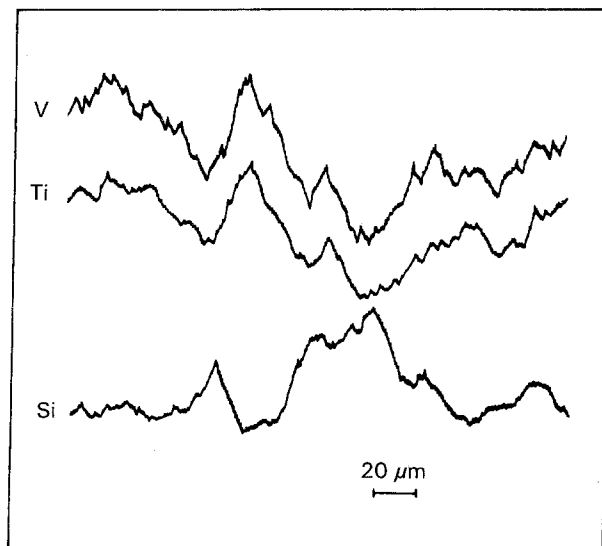
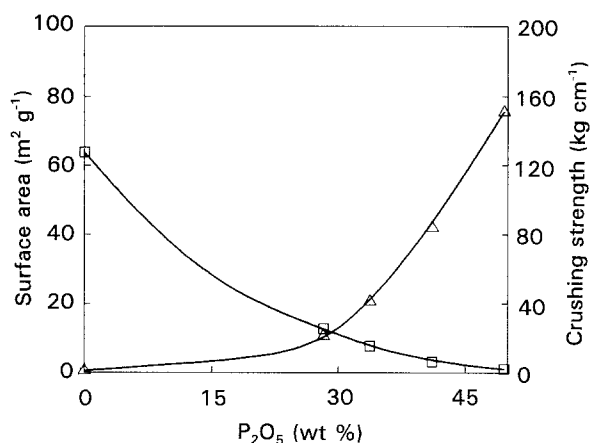*Figure 3* Ti–V–Si line profile for Ti–V–sepiolite catalyst.

Figure 4 Effect of the H_3PO_4 concentration on the ($\triangle$) crushing strength and ($\square$) surface area of Series P catalysts.
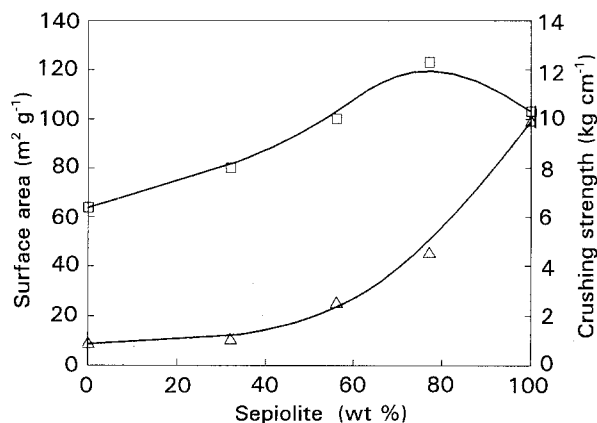

Figure 5 Effect of the sepiolite proportion on the ($\triangle$) crushing strength and ($\square$) surface area of Series S catalysts.

causes an increase in the area, a maximum value being reached when the proportion of sepiolite is between 70 and 90 wt %.

The distribution of pore volume by sizes can be seen in Fig. 6 and later in Fig. 8 for both series of catalysts. The results set out in Fig. 6 show that the greatest contribution of the total pore volume in the
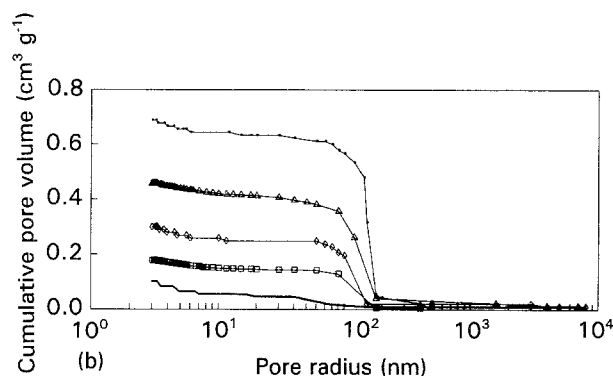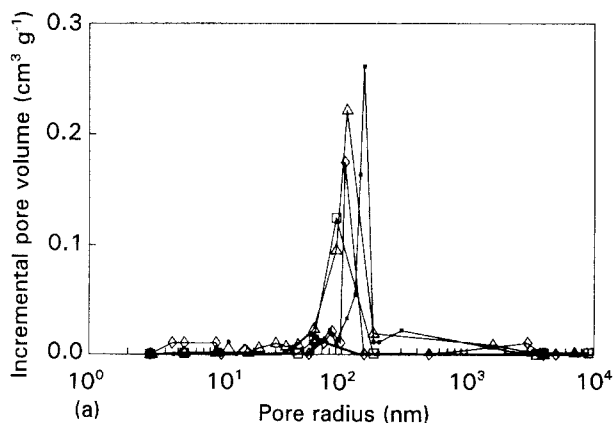

Figure 6 Influence of phosphorus content on the porosity of Series P catalysts. P_2O_5 (wt %): ($\bullet$) 0, ($\triangle$) 28, ($\Diamond$) 34, ($\square$) 41, (———) 50.

TiO_2/V_2O_5 catalyst which does not contain any binder, corresponds to the "pores" with a radius of between 100 and 200 nm. As the concentration of the H_3PO_4 used in the extrusion increases, there is a considerable decrease in the total pore volume, mainly due to the loss of "pores" with a radius of around 100 nm. Bearing in mind that as the average diameter of the starting particles of TiO_2, from SEM analysis, was of the order of 100 nm, the "pores", mentioned previously, would be spaces between the particles of TiO_2. From this, it can be deduced that the H_3PO_4 interacts with the particles of TiO_2 by filling in the interparticulate spaces. Fig. 7 shows a model that describes the binding action of H_3PO_4, as the quantity is increased in this type of catalyst.

When sepiolite is used the pore size distribution can be seen in Fig. 8. If the curve of treated sepiolite is taken as reference, it can be considered that the addition of $TiO_2(+ V_2O_5)$ causes an increase in the pore volume of the sepiolite that seems mainly due to an increase in "pores" with a radius of between 10 and 200 nm. A study of the graphs in Fig. 8b, shows that as the proportion of TiO_2 increases with respect to sepiolite, there is an increase in the average radius of the pores. Taking into account the fibrillar structure of the sepiolite and that the internal channels of the fibres are folded after treatment at 500 °C [6] and, therefore, not accessible to mercury, it can be considered that the greatest contribution to the pore volume in this series of catalysts is due to spaces between fibres or bunches of fibres. These results agree with morphology results yielded by SEM, according to which the structure of this type of catalyst resembles that of sepiolite, but
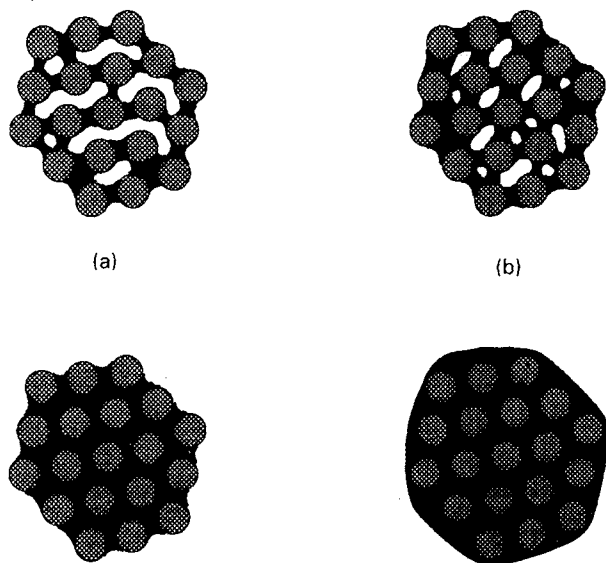
(a)   (b)

Figure 7 Schematic model of the phosphoric acid action as a binder of titania particles. P_2O_5 concentration: (a) 28 %, (b) 34 %, (c) 41 %, and (d) 50 %.
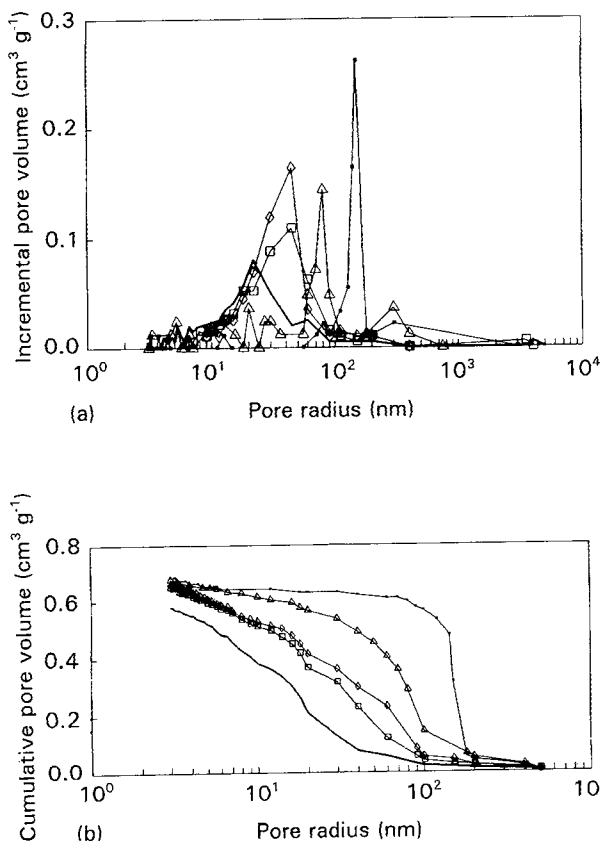

(a)   Pore radius (nm)

(b)   Pore radius (nm)

Figure 8 Influence of sepiolite content on the porosity of Series S catalysts. Sepiolite (wt %): (●) 0, (△) 32, (◇) 56, (□) 77, (——) 100.

the direction of the flow, the reticle which has been formed is destroyed and the particles of TiO_2 are dispersed among the fibres. When the kneading is stopped and during the drying phase, the fibres interact between themselves, giving rise once more to the interfibrillar bonds which give the system its rigidity. During the heat treatment, the fibres tend to fold, "closing" the internal channels of the sepiolite fibres; however, as the TiO_2 particles are scattered among them, there is a greater proportion of interfibrillar spaces. Fig. 9 shows a theoretical model that describes the binding action of sepiolite in this type of catalyst. In it the TiO_2-V_2O_5 particles are scattered between the fibres of the sepiolite that build the skeleton of the catalyst.

3.3. Activity studies in SCR of NO_x with NH_3

The behaviour of the catalysts was studied in the reduction reaction of equimolecular mixtures of NO and NO_2 with NH_3, varying the reaction temperature between 250 and 400 °C, under the operating conditions shown in the Table I.

Fig. 10 shows the variation of the NO_x conversion values at 350 °C as a function of the binder proportion used in the catalyst, which is expressed as weight percentage of sepiolite for the Series S catalysts, and P_2O_5 for the Series P catalysts. When the phosphoric acid, expressed as P_2O_5 wt %, is lower than 30 %, the
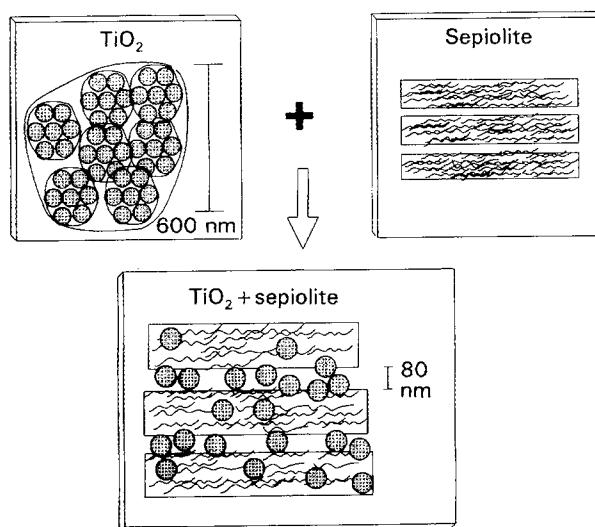

Figure 9 Schematic model of the sepiolite as a binder of titania particles.

with particles of TiO_2 impregnated with V_2O_5, scattered among its fibres. In order to explain this, it can be considered that when a sepiolite gel in water is heavily kneaded, the three-dimensional lattice of the bunch of fibres is destroyed; the latter arranged at random are joined together by bonds of hydrogen bridges between the surface silanol groups [7]. Thus, on shaking the mixture of sepiolite, $TiO_2(+V_2O_5)$ and water briskly, the sepiolite particles point towards

TABLE I. Operating conditions for the activity experiments

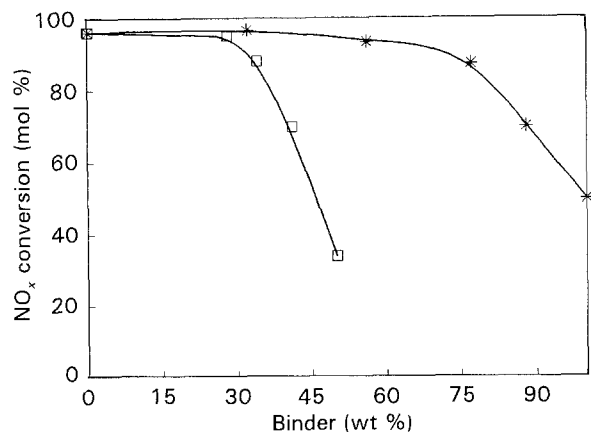| GHSV, STP (h^{-1})	40 000
Reaction temperature (°C)	250–400
Gas composition (p.p.m.)	[NO] = 1500
	$[NO_2]$ = 1500
	$[NH_3]$ = 3000
	$[O_2]$ = 3.0 vol %
	$[N_2]$ = bal.

Figure 10 Effect of the binder concentration on the NO_x conversion values obtained at 350 °C for (□) Series P and (*) Series S catalysts.
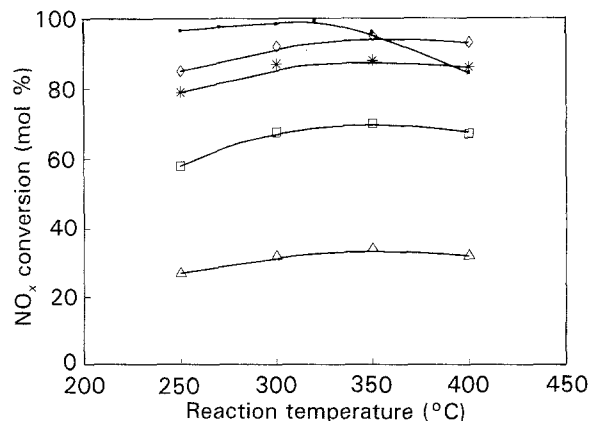

Figure 11 Influence of the reaction temperature on the NO_x conversion obtained with different phosphoric acid concentration (wt %): (■) 0, (◇) 28, (*) 34, (□) 41, (△) 50, expressed as P_2O_5.

NO_x conversion is maintained constant, but higher values of this binder produce a sharp decrease in the NO_x reduction values, while the catalysts prepared with a sepiolite binder, maintain their catalytic activity in acceptable values until a content of 60 wt % of this natural silicate. Above 70 wt % of this silicate in the catalyst, the catalytic activity begins to decrease considerably. However, it should be noted that in the catalyst prepared only with sepiolite, the NO_x reduction is about 50 mol %. The loss in activity which can be seen when the sepiolite proportion is greater than the said value is probably due to the lower concentration of the vanadium in the catalyst.

In order to analyse in detail the effects of both binders, Figs 11 and 12 show the results of the overall conversion of NO_x obtained with the Series P and S catalysts, respectively, as a function of the reaction temperature. In Fig. 11 it can be seen that at reaction temperatures below 350 °C, the catalytic activity decreases as the concentration increases. However, at higher temperatures, the catalysts which have a moderate concentration of H_3PO_4 (P_2O_5 < 35 wt %), give NO_x conversion values which are higher than those of the original V_2O_5/TiO_2. This effect can be explained if they are less active in the oxidation of NH_3 with oxygen, because this reaction is in competition with the reduction of NO_x by NH_3 [8]. This secondary reaction causes the decrease of the NO_x conversion at high temperatures for TiO_2/V_2O_5 catalysts without binder.

The absence of this secondary reaction when phosphoric acid is added to catalysts has been used as the basis for the development of catalysts useful in the removal of NO_x emitted by HNO_3 factories, mainly when the decontamination gases are treated at temperatures above 350 °C [9].

When sepiolite is used, Fig. 12, this effect is not observed and at reaction temperatures above 350 °C the NO_x conversion decreases as the temperature increases. Therefore, it can be considered that the NH_3 oxidation is noticeable. The effect of sepiolite on the catalytic activity can be explained by considering that the sepiolite does not react with the TiO_2 surface and only acts by dispersing the particles of $TiO_2(+V_2O_5)$, in accordance with the model described previously.
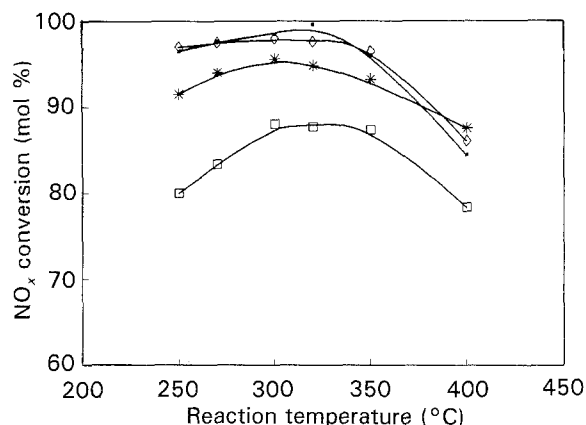

Figure 12 Influence of the temperature on the NO_x conversion values obtained with Series S catalysts. Sepiolite (wt %): (■) 0, (◇) 32, (*) 56, (□) 77.

4. Conclusion

The addition of a binder to the system formed by titanium and vanadium causes significant changes, both in its textural properties, and in its catalytic performance in the selective catalytic reduction of NO_x with NH_3.

The interpretation of the effects produced by phosphoric acid and sepiolite suggests that the compacting process mechanism is different in both cases. The phosphoric acid acts by filling in the spaces between the TiO_2 particles, reacting with its surface and altering its redox properties. The binding action mechanism is similar to that described by Capes as "mobile liquid bonding" [10], where the "skeleton" of the catalyst is formed by TiO_2 particles. The addition of increasing quantities of this binder in the catalyst produces a progressive decrease in the surface area and the pore volume, because it fills in the interparticulate spaces, forming a compact mass in which the active phase is less accessible to the reacting gases. Moreover, the phosphoric acid reacts with TiO_2 and V_2O_5 changing the active phase in such a way that the NH_3 oxidation by oxygen at high temperature, is reduced.

However, when sepiolite is used as binder, the skeleton of the catalyst is formed by the fibrous structure of the silicate and the $TiO_2-V_2O_5$ particles are

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scattered between the fibres in such a way that the catalyst active phase is not changed.

In contradistinction to H_3PO_4, sepiolite causes the compaction of the solid at the same time as it increases the surface area and the dispersion of the active phase and therefore, it can be concluded that this natural silicate is an excellent additive for this kind of catalyst.

Acknowledgement

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