

Effect of titanium-doping on the properties of vanadium antimonate catalysts

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Abstract

Catalysts of nominal compositions $\text{VSb}_{1-x}\text{Ti}_x\text{O}_4$, with $x=0, 0.1, 0.2$ and 0.4 , were prepared by solid state reaction of vanadium(V) oxide, antimony(III) oxide and titanium(IV) oxide mixtures. Their structural and catalytic properties were studied by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), temperature programmed reduction (TPR) and catalytic heterogeneous oxidation of toluene to benzaldehyde.

The samples with 10% ($x=0.1$) and 20% ($x=0.2$) of titanium present the highest activity and selectivity to benzaldehyde under the operating conditions used in this work. When the titanium content is 40% ($x=0.4$), the activity level drops strongly below the level found for the undoped vanadium antimonate. X-ray patterns show the presence of vanadium(V) oxide as a separate phase in this sample, and this is probably the cause of the low catalytic performance.

TPR results show that the replacement of antimony by titanium changes the oxidation-reduction properties of the vanadium antimonate phase.

In the samples with titanium content up to 20%, there seems to be a direct relationship between the selectivity and the separation of the reduction temperatures of both reduction peaks of the TPR profile: the larger the separation, the higher is the selectivity to benzaldehyde.

All the samples with $x=0, 0.1$ and 0.2 show surface antimony excess despite being prepared from stoichiometric mixtures of nominal V/Sb ratios larger than or equal to 1. ©2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The selective oxidation of toluene remains far from commercial production because of the low toluene conversion and the poor benzaldehyde selectivity. At present, vanadium oxide, commonly used for partial oxidation of aromatic hydrocarbons, is widely used

as a catalyst in the partial oxidation of toluene. The presence of promoters can influence the activities of this catalyst [1]. Vanadium–titanium catalysts modified with SeO_2 , TeO_2 , and Sb_2O_3 have been found to be very effective in the selective oxidation of toluene due to the enhancement of catalyst performance in terms of toluene conversion and benzoic acid selectivity [2]. Germain and Laugier [3–5] have reported the oxidation of toluene over series of pure oxides and oxides mixtures. The mixtures Fe–Mo–O, Sb–Mo–O,

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U–Mo–O and Sb–Mo–O gave the best results, exhibiting good activity and selectivity.

Likewise, antimony oxides stabilized in matrices with a rutile structure have been used as catalysts for olefine (amm)oxidations showing high activity and selectivity [6]. Grasselli [7] reported that xylenes can be (amm)oxidized using a catalyst based on vanadium oxides strongly doped, particularly, with Sb, Nb and Cs. He suggested that VSbO₄ is one of the phases formed, thus resulting in a more selective catalyst.

In the last few years, catalysts based on vanadium–antimony oxides, applied to (amm)oxidation reactions, have been widely studied [8,9], and many patents have been published using VSbO₄ as the active phase [10,11].

The synthesis of VSbO₄ by solid state reaction of vanadium(V) oxide and antimony(III) oxide has been analyzed by Berry et al. [12–14] and Birchall and Sleight [15]. They have proposed a rutile-related phase with composition V_{1–y}Sb_{1–y}O₄ (0 < y < 0.1) in the solid prepared in air. The solid state reaction between vanadium and antimony involves a two-electron redox reaction between V⁵⁺ and Sb³⁺ to form the VSbO₄ rutile phase. Birchall and Sleight [15], from Sb Mössbauer results, have identified Sb(V) in the rutile phase. Therefore, based on charge balance, vanadium is formally present as V(III). However, due to the easy non-stoichiometry of the rutile phase and the possible intergrowth of the isostructural V⁴⁺ oxide, the VSbO₄ may be better described as (V³⁺–V⁴⁺)_{1–y}Sb_{1–y}O₄ [16].

The study of this system appears to be very complex since several different species are available on the surface as possible active sites for catalytic reaction. Thus, the activity and selectivity of VSbO₄ in catalytic oxidation can be affected by the V³⁺/V⁴⁺ and Sb³⁺/Sb⁵⁺ ratios [8]. The introduction of foreign ions in order to modify these ratios could be a key for improving the catalytic performance. In this sense, Berry et al. [17] prepared titanium-substituted vanadium antimonates and studied their structural properties. The X-ray diffraction (XRD) patterns showed a contraction in the lattice parameters as Sb⁵⁺ is replaced by Ti⁴⁺, with concomitant loss of oxygen and oxidation of V(III) to V(IV), as an indication of the incorporation of Ti within the rutile-related phase. They suggested that

this material might have promising properties as a catalyst for selective oxidation reactions. Nevertheless, they were never tested in catalytic oxidation reactions.

In this work, the changes produced on the structure and the reactivity of vanadium antimonate by replacing the antimony sites with titanium were studied by XRD, X-ray photoelectron spectroscopy (XPS) and temperature programmed reduction (TPR) techniques and gas-phase oxidation of toluene as the test catalytic reaction.

2. Experimental

2.1. Catalyst preparation

The catalysts were prepared according to the method published by Berry et al. [17], by mechanical mixing of pure vanadium(V) oxide, antimony(III) oxide and titanium(IV) oxide (Mallinckrodt reagent grade). The amounts of each oxide in the sample corresponded to those necessary to obtain a stoichiometric solid of composition VSb_{1–x}Ti_xO₄ (with x = 0, 0.1, 0.2 and 0.4). The reactant powders (2 g) were gently grinded in order to have good mixing but avoiding mechanicochemical alterations. The powders were put into quartz crucibles and heated in air in a conventional furnace according to the following schedule: heating from 25 to 600°C over 10 h, temperature kept at 600°C during 12 h, heating from 600 to 750°C over 6 h, temperature kept at 750°C during 9 h, furnace cooling down.

2.2. Catalyst characterization

X-ray powder diffraction (XRD) measurements were carried out on a Rigaku diffractometer using Cu K α radiation.

TPR was performed with a thermal conductivity detector, on samples of 20 mg, in a 98% (molar) nitrogen–2% (molar) hydrogen gas mixture, using a gas flow rate of 120 cm³/min and a temperature ramp rate of 10°C/min.

XPS measurements were carried out with an ESCA 750 Shimadzu Electron Spectrometer. Non-monochromatic Mg K α X-ray radiation was used. The

anode was operated at 8 kV and 30 mA and the pressure in the analysis chamber was about 2×10^{-6} Pa. Spectra were collected for the spectral regions corresponding to O 1s, Sb 3d, V 2p, C 1s and Ti 2p. The C 1s signal was adjusted to a position of 284.6 eV.

In addition, surface areas were measured by the BET method using N_2 adsorption at 77 K in a Micromeritics Gemini 2360.

2.3. Catalytic tests

Toluene oxidation was carried out in a conventional flow reactor operated isothermally at atmospheric pressure.

The reactor was made with a Pyrex glass tube of 13 mm inner diameter. Toluene was fed by means of a carrier air stream flowing through a saturator. The feed toluene/air molar ratio was controlled by adjusting both the saturator temperature and the input air flow rate. The reaction temperature was measured with a sliding thermocouple placed inside the bed. Since the oxidation reactions are highly exothermic, the catalyst bed was diluted (1 : 10) with glass particles, of the same diameter range, in order to avoid adverse thermal effects.

The composition of the input and output streams were analyzed by on-line gas chromatography. An HP 6890, equipped with an FID detector and an HP INNOWAX 30 m \times 320 μ m \times 0.25 μ m polyethylenglycol column was used to analyze the concentrations of toluene in the feed and the output streams, and the concentration of partial oxidation products in the output. The composition of the total oxidation products was determined with a Shimadzu GC 8A chromatograph equipped with a TCD detector and Porapak Q 2m/Molecular Sieve 5A columns.

Selectivities to benzaldehyde were calculated as mole of products \times number of C atoms in the product/mole of toluene converted \times 7.

The reactor was operated in steady-state conditions. The catalytic tests were performed under the following conditions: catalyst mass: 100–500 mg; temperature: 713 K; total feed rate: 200–500 ml/min; toluene molar fraction: 0.0086; oxygen molar fraction: 0.1983 (nitrogen balance); particle diameter < 120 μ m.

3. Results

3.1. XRD

The X-ray powder diffraction data indicate the rutile-related $VSb_{1-x}Ti_xO_4$ phase (where $x = 0, 0.1, 0.2$ and 0.4) to be similar to that formerly described as $VSbO_4$ containing vanadium(III) and antimony(V) [12,17]. The absence of lines associated with titanium(IV) oxide is related to the incorporation of titanium within the rutile phase. In addition, the $VSb_{0.6}Ti_{0.4}O_4$ XRD pattern shows the presence of small quantities of crystalline vanadium(V) oxide. This oxide is segregated because there is not enough Sb_2O_3 in the starting mixtures to reduce all the V^{5+} to V^{3+} and to incorporate it within the rutile phase.

3.2. TPR

TPR profiles of the catalysts prepared, pure V_2O_5 and V_2O_5 – $VSbO_4$ solid mixture are shown in Fig. 1. It can be seen that all the catalysts prepared show two peaks pointing out that there are two centers of reduction. TPR profile for the sample with $x = 0.4$ shows a third peak between the former two.

In the titanium-doped samples, the first TPR peak appears at lower temperatures than in the undoped one. On the contrary, the second peak appears at slightly higher temperatures. Therefore, the temperature difference corresponding to the first and the second peak is higher in the titanium-doped samples. The analysis of the TPR profiles recorded for V_2O_5 and V_2O_5 – $VSbO_4$ solid mixture suggests that the third peak appearing for sample with 40% of titanium content can be associated with the reduction of V^{5+} . The temperatures of the reduction peaks are summarized in Table 1.

3.3. XPS

In Table 2, there is a summary of the binding energies of V 2p 3/2, Sb 3d 3/2 and Ti 2p 3/2 referred to the C 1s peak. The O 1s and Sb 3d 5/2 signals are superimposed, and therefore, only the Sb 3d 3/2 signal is reported. Values within round brackets represent the corresponding full-width-at-half-maximum (FWHM).

The analysis of the valence states of Sb and V is difficult to perform since the differences between the

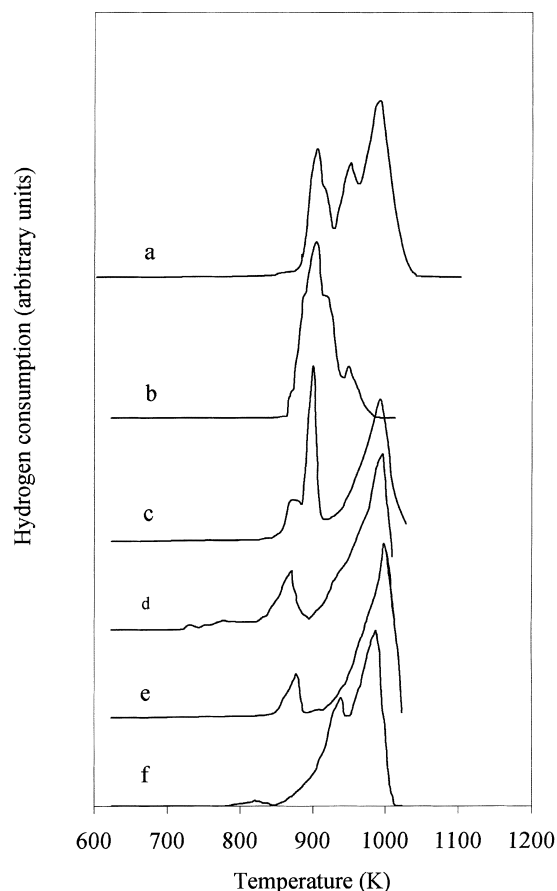


Fig. 1. TPR profiles: (a) $V_2O_5 + VSbO_4$; (b) V_2O_5 ; (c) $VSb_{0.6}Ti_{0.4}O_4$; (d) $VSb_{0.8}Ti_{0.2}O_4$; (e) $VSb_{0.9}Ti_{0.1}O_4$; (f) $VSbO_4$.

binding energies corresponding to the oxidation states are approximately 0.8 eV for each metal. Nevertheless, the antimony on the solid surface may be considered in terms of the Sb 3d 3/2 binding energies. For all the

Table 1
TPR temperature of reduction peaks

Sample	T_1 (K)	T_2 (K)	ΔT (K) = ($T_1 - T_2$)
	First peak	Second peak	
$VSbO_4$	939	987	52
$VSb_{0.9}Ti_{0.1}O_4$	877	997	120
$VSb_{0.8}Ti_{0.2}O_4$	871	996	125
$VSb_{0.6}Ti_{0.4}O_4$	872	992	120
$VSb_{0.6}Ti_{0.4}O_4$	Third peak	900 K	
$V_2O_5/VSbO_4$	Third peak	905 K	
V_2O_5	Primary peak	904 K	

Table 2
Binding energies and FWHM. C 1s binding energy reference: 284.6 eV

Sample	V 2p 3/2	Sb 3d 3/2	Ti 2p 3/2
$VSbO_4$	516.3 (2.3)	539.9 (1.9)	–
$VSb_{0.9}Ti_{0.1}O_4$	516.4 (2.2)	539.9 (1.8)	458.1 (2.4)
$VSb_{0.8}Ti_{0.2}O_4$	516.3 (2.2)	539.5 (1.8)	457.96 (1.8)
$VSb_{0.6}Ti_{0.4}O_4$	516.6 (1.7)	539.7 (1.8)	458.2 (2.3)

materials, the values fall within the range 539.5–539.9 eV. If the binding energy values obtained in this work are compared with those reported by other authors [18,19] (Sb_2O_3 : 539.0, 538.9 eV; Sb_2O_5 : 539.8, 540.2 eV, respectively, after conversion to the C1s reference value used in the present study), it may be concluded that Sb^{5+} predominates on the surface. On the other hand, the presence of Sb^{3+} should not be discarded because the Sb(III) with coordination number 4 would be placed more easily on the surface of a rutile structure, as has been proposed by Berry [20] and Allen and Bowker [21].

The binding energies obtained for the V 2p 3/2 peak in this work are smaller than those reported previously for vanadium(V), but are higher than those reported for V(IV) and V(III) [22] (516.9, 515.9 and 515.7 eV, respectively, after conversion to the C1s reference value used in the present study). It may be concluded that V(V) and V(IV) are present on the surface, but it is not possible to discard the presence of V(III). The presence of vanadium(V) on the surface suggests the formation of an amorphous phase of V_2O_5 , not detectable by XRD, due to the incomplete reaction of antimony with vanadium to form vanadium antimonate. Similar results were obtained by other researchers [16]. Particularly, the 40% titanium sample presents a slight increase in the binding energy and a narrower FWHM value, indicating a greater contribution of vanadium(V) on the surface. This is in accordance with the V_2O_5 phase detected by XRD and the third TPR peak associated with this phase, as discussed above.

Table 3 shows the surface atomic ratios for the fresh samples. It can be noted that the V/Sb and V/Ti surface atomic ratios do not change with an increase in titanium content up to 20%. Likewise, the V/Sb surface ratios are lower than 1, indicating that there is an excess of Sb on the surface even in samples with nominal composition V/Sb > 1.

Table 3
Surface atomic ratios

Sample	V/Sb	Nominal V/Sb	V/Ti ratio	Sb/Ti ratio
VSbO ₄	0.6	1	–	–
VSb _{0.9} Ti _{0.1} O ₄	0.7	1.11	2.8	4
VSb _{0.8} Ti _{0.2} O ₄	0.63	1.25	2.86	4.1
VSb _{0.6} Ti _{0.4} O ₄	1.1	1.67	4.5	4.5

On the other hand, in the sample with 40% of titanium, these atomic ratios increase significantly, due to a larger vanadium contribution on the surface. Again, the findings are in agreement with the vanadium(V) oxide phase detected in XRD patterns, the third TPR peak and the slight increase in the XPS binding energy.

Despite the increase in titanium content, all the samples have the same Sb/Ti surface ratio.

3.4. Catalytic tests

Previous catalytic tests performed at different reaction temperatures have shown that the toluene conversion starts at 563 K, with CO₂, CO and benzaldehyde being the main products.

In order to ensure that the kinetic experiments provide meaningful results, preliminary catalytic tests were carried out at different residence times, particle

diameters and total gas flows. Some of them were performed without catalyst in order to verify the absence of the thermal oxidation. These tests showed a negligible contribution of homogeneous oxidation. The absence of internal and external diffusion limitations, for particle diameters below 120 μm and total gas flow equal or greater than 100 ml/min was confirmed. Non-pretreated catalyst showed stable activity during a typical run period of 12 h.

The catalytic experiments were carried out in integral reactor conditions, keeping the feed composition and the temperature constant while varying the space-time. Thus, the conversion of toluene was a simple measure to compare the activity of different catalysts in the reaction studied.

The results are plotted in Fig. 2 for the samples with different titanium contents. A slight increase in toluene conversion with an increase in titanium content up to 20% can be observed. When the titanium concentration is 40%, there is a large decrease in the reaction rate. This activity drop is not related to a change in the specific surface area since all samples have shown similar surface areas (1 m²/g).

Fig. 3 presents the benzaldehyde selectivity versus toluene conversion. At the same conversion, the samples with 10 and 20% of titanium content present the same benzaldehyde selectivity which are the largest observed. The sample with 40% of titanium content

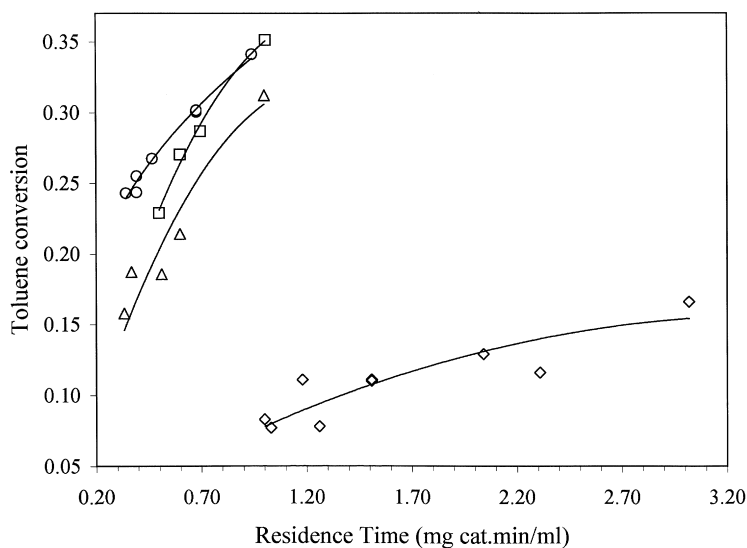


Fig. 2. Toluene conversion vs. residence time. Samples' symbols: Δ: VSbO₄; □: VSb_{0.9}Ti_{0.1}O₄; ○: VSb_{0.8}Ti_{0.2}O₄; ◇: VSb_{0.6}Ti_{0.4}O₄.

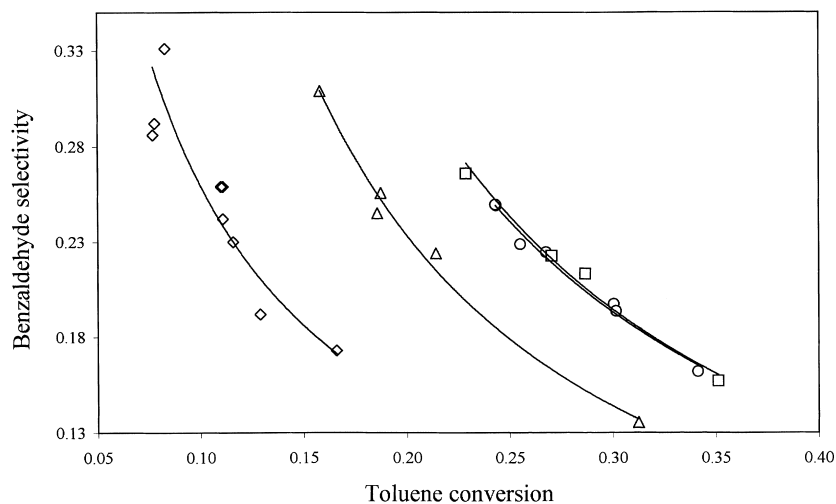


Fig. 3. Benzaldehyde selectivity vs. toluene conversion. Samples' symbols: Δ : VSbO₄; \square : VSb_{0.9}Ti_{0.1}O₄; \circ : VSb_{0.8}Ti_{0.2}O₄; \diamond : VSb_{0.6}Ti_{0.4}O₄.

shows a selectivity value smaller than that of the undoped one.

4. Discussion

XRD studies show that the antimony substitution by titanium in the rutile phase with nominal composition VSb_{1-x}Ti_xO₄ ($x = 0, 0.1, 0.2$ and 0.4) incorporates the titanium cation.

The catalysts doped with titanium content up to 20% and the undoped sample show surface antimony excess despite of being prepared from stoichiometric mixtures of nominal V/Sb ratios larger than or equal to 1. The V/Sb surface ratios for these samples have the same values. This means that the addition of titanium up to 20% is counterbalanced by changes in the oxidation states of vanadium and antimony in the bulk, so that the V/Sb surface atomic ratio remains constant. However, TPR profiles exhibit remarkable differences. The samples with titanium contents of 10 and 20% have the first peak of reduction at a lower temperature than that in the case of the undoped one. This lower reduction temperature would be responsible for the higher catalytic activity in the oxidation of toluene (Fig. 2). These samples also have higher selectivity to partial oxidation products, when compared with the undoped one at the same conversion level

(Fig. 3). This enhancement could not be explained as a consequence of a change in the V/Sb surface ratio since this ratio does not change noticeably (Table 3). There is no strong change in the oxidation states of the surface cations either since the V 2p 3/2 and Sb 3d 3/2 signals are similar, as can be seen from the binding energies and the FWHM values given in Table 2. On the other hand, it is possible to speculate that the lower reduction temperature of the first TPR peak and the slight increase in the temperature of the second peak are an indication that the reduced state of the low-temperature peak and the oxidized state of the high-temperature peak would be stabilized on the surface of the working catalyst. Then, an efficient redox system for electron transfer would be achieved. [23] Therefore, the replacement of Sb(V) by Ti(IV) up to 20% improves the benzaldehyde selectivity due to a change in the redox properties of the rutile phase.

In the XRD pattern of the sample with 40% of titanium, a small content of vanadium(V) oxide is detected. The presence of this V₂O₅ phase determines the appearance of a new peak in the TPR profile, a change in the V/Sb surface atomic ratio and a large change in the catalytic behaviour. This phase would be responsible for the drop in activity and selectivity levels, which is in agreement with the findings of other researchers [1] indicating that the segregation of crystalline V₂O₅ on TiO₂ surface leads to lower

conversion of toluene and worse selectivity to partial oxidation products.

5. Conclusions

The results obtained show that vanadium antimonate oxide can be an effective catalyst for the selective oxidation of toluene to benzaldehyde. The addition of titanium, at concentration levels which do not produce segregation of a crystalline V_2O_5 phase, improves the catalytic performance, particularly the benzaldehyde selectivity, due to a change in the redox properties of the solid.

When crystalline V_2O_5 phase, detectable by XRD, is formed, the toluene conversion and the benzaldehyde selectivity drop sharply. Thus, this oxide is probably responsible for the poorer catalytic behaviour.

Acknowledgements

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