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Catalytic behaviour of V-Sb-Ti mixed oxides in the vapour-phase reaction of ethylbenzene with air

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Abstract

The objective of this work is to study the behaviour of V-Sb-Ti mixed oxides in the ODH of ethylbenzene and to compare these results with those previously reported for the partial oxidation of toluene with the same catalysts. The solids, with nominal compositions $VSbO_4$, $VSb_{0.8}Ti_{0.2}O_4$ and $V_{0.8}SbTi_{0.2}O_4$, were prepared by solid-state reaction. Catalytic tests were carried out in a fixed-bed reactor using ethylbenzene and air as reactants.

A relation between the dehydrogenation function of the solids and their Sb/V surface ratios was established. The higher Sb/V surface ratio the higher selectivity to styrene but pointing out the participation of Sb sites in the H-abstraction step.

Comparison between toluene and ethylbenzene oxidation results has confirmed that the reaction rate is independent of the hydrocarbon used in the feed and controlled by the reoxidation of the catalyst. Besides, at the same conversion level, selectivity to total oxidation products is lower when ethylbenzene is used as reactant, due to the formation of a stable dehydrogenated product, styrene, which competes with oxygen for the chemisorption on Lewis acid sites.

Keywords: Vanadium antimonate; ODH; Ethylbenzene; Toluene

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1. Introduction

It is known that hydrocarbon oxidations catalysed by mixed oxides are carried out through three reaction steps: (1) the abstraction of the hydrocarbon hydrogen, (2) the insertion of the lattice oxygen in the dehydrogenated intermediate to produce the oxidised compound and (3) the insertion of gaseous oxygen in the solid catalyst as lattice oxygen.

In previous work [1–4], we have studied the selective oxidation of toluene on $VSbO_4$ catalyst partially substituted by Ti in order to elucidate the role of Sb and V as active sites of the reaction. The results obtained allowed for the proposal that V^{4+} is involved in the incorporation of gaseous oxygen as lattice oxygen and hold Sb sites in an oxidation sate (Sb^{5+}) high enough to insert the lattice oxygen in the toluene molecule. Since the dehydrogenation product of toluene is not stable it was not possible to analyse the participation of Sb or V in the hydrogen-abstraction step. On the other hand, our theoretical studies [4,5] have shown that, during toluene parallel adsorption on Sb–Sb or Sb–V sites, a bonding interaction between one H-atom of the methyl group with a Sb-cation is established. Thus, H approaches to a Sb–O centre and C–H bond is broken. Thus, there are theoretical evidences that Sb-cation participates in the H-abstraction step (ODH) to give benzyl-type species.

On the other hand, the H-abstraction from ethylbenzene produces styrene, which is a stable compound that can be detected by chromatography analysis.

The industrial processes for styrene production are based on the catalytic dehydrogenation of ethylbenzene, which is an endothermic reaction with its conversion limited by

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Nomenclature

F_{HC}	molar flux of the hydrocarbon reactant in the outlet
$F^{\mathrm{o}}_{\mathrm{HC}}$	molar flux of the hydrocarbon reactant in the feed
F_P	molar flux of product *P* in the outlet
$N^{\mathrm{C}}_{\mathrm{HC}}$	number of C atoms in the hydrocarbon used as the reactant
$N^{\mathrm{C}}_{\mathrm{P}}$	number of C atoms in product *P*
R_P	yield to product *P* in molar percentage
S_P	selectivity to product *P* in molar percentage
X_{HC}	hydrocarbon molar conversion in molar percentage
Greek letter	
τ	space–time

thermodynamic equilibrium. Thus, operating conditions of commercial processes involve high reaction temperatures (600–630 °C) and low ethylbenzene pressure [6]. Since the process is equilibrium-limited and energy intensive, there is a great interest for the development of an oxidative dehydrogenation (ODH) process as an alternative to produce styrene. The ODH reaction is exothermic and has nothermodynamic restrictions.

ODH reactions are also receiving great attention in the synthesis of valuable alkenes but, the finding of efficient catalysts with good olefin production is still a critical point and these processes are still far from being widely used at industrial-scale.

Juarez López et al. [7] have studied a series of alumina supported MVSb oxides, with M: Ni, Co, Bi or Sn, in the ODH of ethane. They have concluded that the presence of free vanadium and nickel oxides in the catalyst negatively influenced the selectivity over the dehydrogenation product.

Mamedov et al. [8] carried out the characterization and evaluation of MVSb mixed oxides, where M is Ni, Co, Bi or Sn, supported on alumina, for the ODH of light paraffins, ethylbenzene and ethanol. They have found that the most selective catalyst was the most easily reduced NiVSb solid, relating the selectivity to the dehydrogenated product with the redox properties.

Blasco and López Nieto [9] have summarized the main data reported in the last years on ODH on vanadium oxides. They have concluded that the coordination number, the aggregation state of vanadium oxide surface species and the presence of acid–base sites are important factors that must be considered to develop selective catalysts in ODH reactions.

Vislovskiy et al. [10] have concluded that alumina-supported vanadium-containing oxides are active and selective in the ODH of light alkanes. They have also found that the amount of active oxygen species and their reactivity in redox transformations is improved by doping the catalyst with antimony.

Bychkov et al. [11] have studied the properties of lattice oxygen in vanadium-containing supported catalyst for ODH of paraffins C2–C4. They have found evidences that the process takes place via a stepwise redox mechanism with the participation of catalyst lattice-oxygen. The addition of antimony increases the amount of reactive oxygen, which accelerates redox processes.

In summary, VSb oxides are known to be very efficient as catalyst for ODH of paraffins. Nevertheless, only few studies in the literature have explained the role of each component in the reaction.

The objective of this work is to analyse the behaviour of V-Sb-Ti mixed oxides in the ODH of ethylbenzene and to compare the results with those previously reported for the partial oxidation of toluene with the same catalysts.

2. Experimental

2.1. Catalyst preparation and characterization

The catalysts were prepared by solid-state reaction of powders obtained by mechanical mixing of the pure oxides. The preparation method and the results of the characterization of the solids by sorptometry, X-ray powder diffraction (XRD) and X-ray photoelectron spectroscopy (XPS), were published in previous work [1,2]. TPR experiments were 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 cm^3/min and a temperature ramp-rate of 10 °C/min.

Nominal compositions of the catalysts prepared were $\mathrm{VSbO_4}$, $\mathrm{VSb_{0.8}Ti_{0.2}O_4}$ and $\mathrm{V_{0.8}SbTi_{0.2}O_4}$. These samples are identified as *VSb*, *Sb08* and *V08*, respectively.

2.2. Catalytic tests

Catalytic tests were carried out in a conventional flow reactor operated at 440 °C and at atmospheric pressure. The reactor was made with a Pyrex glass tube of 13 mm inner diameter. Input and output lines are heated in order to avoid condensation of reactants or products. Since oxidation and dehydrogenation reactions are highly exothermal, the catalyst bed was diluted with glass particles of the same diameter range, in a 1/10 mass ratio.

Composition of input and output streams is analysed by on-line gas chromatography using a HP 6890 GC, equipped with FID and TCD detectors. FID detector coupled with a HP INNOWAX 30 m × 320 μm × 0.25 μm polyethylenglycol column was used to determine the concentrations of ethylbenzene in the feed and products (except carbon oxides) in the outlet, while TCD detector coupled with a CTR1 6 ft × 1/4 in. column was used to determine carbon oxides and oxygen concentrations in the outlet stream.

Ethylbenzene conversion in molar percentage (X_{EB}) was calculated as:

$$\frac{F^{\mathrm{o}}_{\mathrm{EB}} - F_{\mathrm{EB}}}{F^{\mathrm{o}}_{\mathrm{EB}}} \times 100.$$

Selectivity to a specific product in molar percentage (S_P) was calculated as:

$$\frac{F_P \times N_P^{\mathrm{C}} \times 100}{(F^{\mathrm{o}}_{\mathrm{EB}} - F_{\mathrm{EB}}) \times N_{\mathrm{EB}}^{\mathrm{C}}}.$$

In this way the sum of all selectivities must equal 100.

Product yields in molar percentage (R_P) are calculated as:

$$\frac{F_P \times N_P^{\mathrm{C}} \times 100}{F^{\mathrm{o}}_{\mathrm{EB}} \times N_{\mathrm{EB}}^{\mathrm{C}}}$$

Space–time (τ) is defined as (catalyst mass/total flow rate).

Due to the low molar fraction of ethylbenzene in the feed, the flow rate is almost constant.

Previous catalytic tests were performed in order to determine the operating conditions that ensure negligible contribution of homogeneous reactions (less than 1% in all cases) and absence of internal and external diffusion limitations.

The catalytic tests were performed under the following conditions, total flow rate: 400 $\mathrm{cm^3/min}$ (at 25 °C and 1 atm); catalyst mass: 80, 160 and 240 mg; feed composition: ethylbenzene molar fraction, 0.008 ± 0.0002; oxygen molar fraction, 0.21 ± 0.007 and nitrogen balance; particle diameter: <120 μm.

3. Results and discussion

TPR profiles are plotted in Fig. 1. They show that samples VSb and Sb08 have two centres of reduction while sample V08 has only one. Comparing the TPR profiles of the samples with those of the pure oxides and the VSb + V_2O_5 mechanical mixture, it is clear that the TPR signals of VSb, Sb08 and V08 samples represent the behaviour of the redox couples in the antimonate rutile-phase [12].

It can be seen that in sample Sb08, the first peak occurs at a lower temperature and the second peak slightly moves at a higher temperature when comparing with the undoped sample. On the other hand, when V is replaced by Ti (sample V08) the TPR profile shows only one peak pointing out that the first centre of reduction is either completely reduced or the two signals are superimposed in one peak. Besides, the temperature value of the peak maximum falls between those obtained for the two centres of the undoped sample.

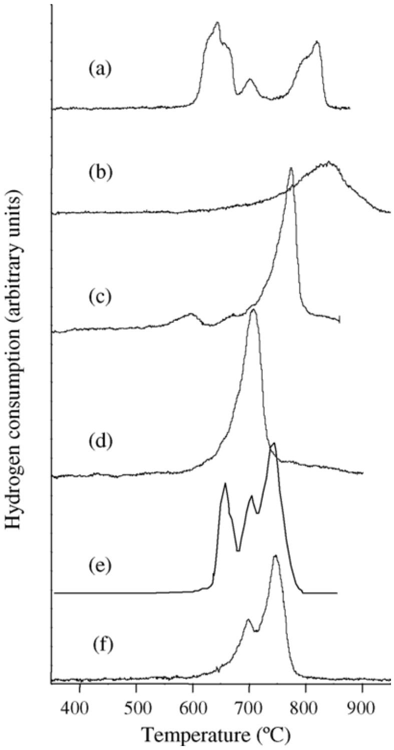

Fig. 1. TPR profiles for samples and pure oxides: (a) V_2O_5, (b) Sb_2O_4, (c) Sb08, (d) V08, (e) VSb + V_2O_5 (mechanical mixture) and (f) VSb.

It can be concluded, as it was reported in a previous work [2,4] that the TPR profiles of the three samples: VSb, V08 and Sb08 show the reduction of V^{4+} and Sb^{5+} sites present in the rutile structure. The main peak corresponds to the reduction of Sb^{5+} while the secondary one is related with V^{4+} reduction. The partial substitution of Sb by Ti in sample Sb08 promotes the V^{3+} oxidation to V^{4+} [2]. Therefore, Sb^{5+} is stabilized in the rutile-phase and its reduction becomes more difficult. As a consequence of that, the difference between both reduction potentials increases promoting a more efficient electron transfer between V and Sb sites in the rutile structure.

In Fig. 2, the conversion of ethylbenzene is plotted as a function of the time-on-stream, at the lower space–time, for the three catalysts. It can be observed that there is a stable behaviour of the catalysts after an initial period of induction. Sb08 sample reaches the stable condition in a shorter time than V08 and VSb ones. During the initial induction period the catalyst surface changes till reaching a stable condition.

Satisfactory carbon balances (±5%) between reactor inlet and outlet, were observed in all the experiments performed. The products obtained were: styrene, benzaldehyde, benzoic acid, carbon dioxide and carbon monoxide, being benzoic acid the main product for all catalyst studied, instead of benzaldehyde as it was observed in the case of toluene oxidation [1,2].

Other researchers [13,14] have reported, for de-ODH of ethylbenzene, an important increasing of styrene yield with time-on-stream. They consider that this fact is caused by the

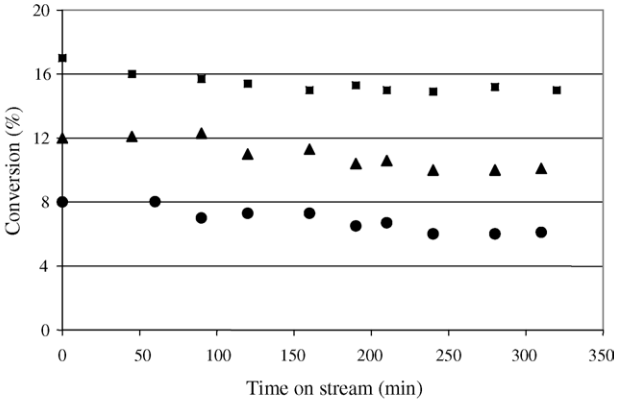

Fig. 2. Ethylbenzene conversion vs. time on stream for the different samples: (●) Sb08, (■) VSb and (▲) V08.

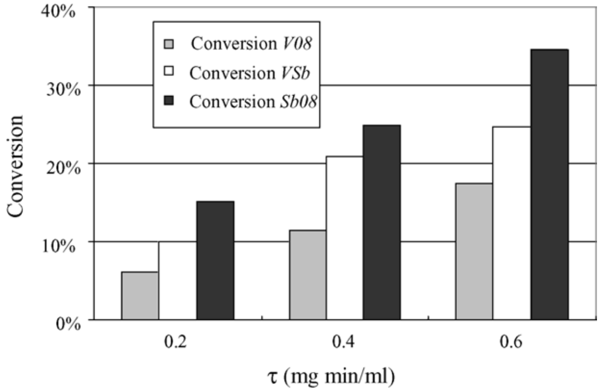

Fig. 4. Ethylbenzene conversion vs. space–time for the different samples.

deposition of carbonaceous solids over the catalyst that, instead of causing deactivation, catalyses the ODH reaction. Therefore, after a first period of induction, the actual catalyst would be the carbonaceous deposit instead of the original one. In order to dismiss the occurrence of this situation, yields to styrene as a function of time-on-stream, for the three solids and one space–time condition, are plotted in Fig. 3. It is clear from Fig. 3 that yields to styrene have not shown an increase with time-on-stream. The same situation has been observed at other space–times. These results allow us to dismiss the possible participation of carbonaceous deposits as ODH actives sites.

In the following paragraphs the results corresponding to the stabilized condition of the catalyst surface are presented.

In Fig. 4, ethylbenzene conversion is plotted as a function of space–time for the three catalysts. Due to the fact that all the solids have the same specific surface (1 m^2/g) [1,2], it is clear that activity increases in the order V08, VSb and Sb08 for all space–times. The same behaviour was observed in the case of toluene oxidation [1,2].

In Fig. 5, ethylbenzene conversion is plotted as a function of V/Sb nominal ratio for three different space–times. In this figure, trend lines represent the results previously reported in toluene oxidation employing the same operating conditions [2]. This figure points out two important conclusions: (i) the conversion is independent of the hydrocarbon used, since toluene and ethylbenzene conversions present similar values for the same catalyst and space–time condition; (ii) the conversion is directly related with V/Sb nominal ratio in the solid. In any process involving chemical reactions, conversion depends on the operating conditions (temperature, space–time, feed composition, etc.) and the intrinsic kinetic of the whole process. Moreover, the reaction rate of the whole process, which is composed by the different reactions steps with their corresponding kinetics, is determined by the rate of the limiting-step. Thus, Fig. 5 is showing that the same limiting step determines the kinetic of the whole process, and this limiting step is directly related with V/Sb nominal ratio. These results allow us to confirm that, as it was previously reported [2], catalyst reoxidation is the rate-limiting step and both metals (V and Sb) in the bulk participate in the solid reoxidation mechanism. In the literature, other authors have proposed that the limiting step in alkane oxidation or ODH, is the H-abstraction [17]. We think that the different behaviour observed in our experiments is due to the presence of the aromatic ring in the reactant molecule with a

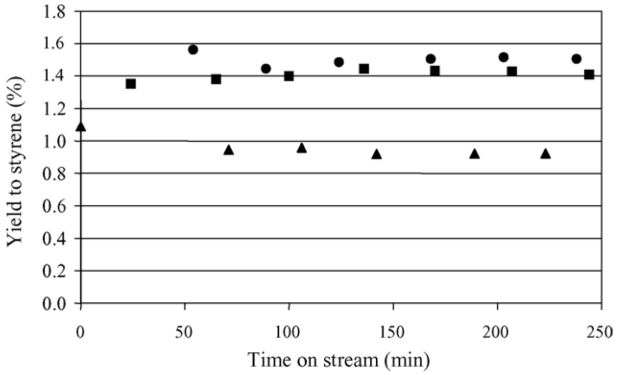

Fig. 3. Yield to styrene vs. time on stream for the different samples: (●) Sb08, (■) VSb and (▲) V08.

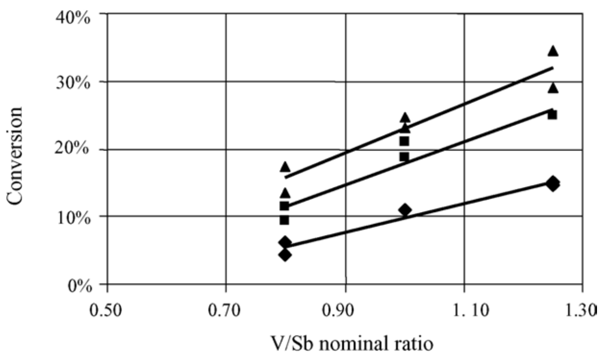

Fig. 5. Conversion vs. V/Sb nominal ratio. (◆) $\tau = 0.2$ mg min/ml, (■) $\tau = 0.4$ mg min/ml and (▲) $\tau = 0.6$ mg min/ml.

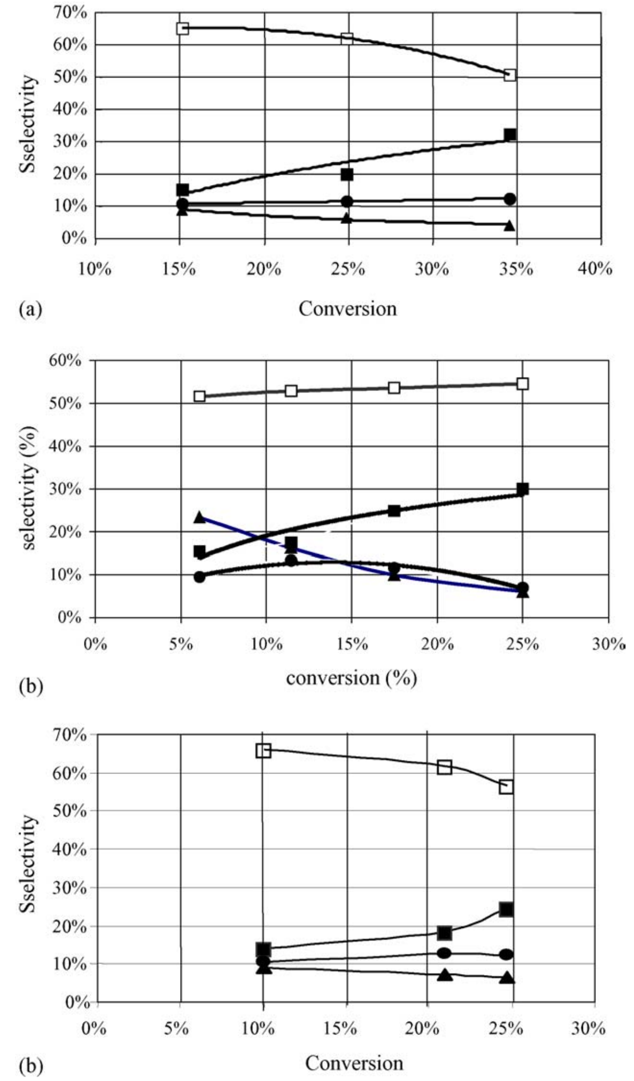

Fig. 6. (a) Product selectivity vs. ethylbenzene conversion for Sb08 sample: (□) benzoic acid selectivity, (■) CO_x selectivity, (●) benzaldehyde selectivity and (▲) styrene selectivity. (b) Product selectivity vs. ethylbenzene conversion for V08 sample: (□) benzoic acid selectivity, (■) CO_x selectivity, (●) benzaldehyde selectivity and (▲) styrene selectivity. (c) Product selectivity vs. ethylbenzene conversion for VSb sample: (□) benzoic acid selectivity, (■) CO_x selectivity, (●) benzaldehyde selectivity and (▲) styrene selectivity.

stronger adsorption on the catalytic surface than an alkane [18].

In Fig. 6, product selectivities are plotted as a function of ethylbenzene conversion for samples Sb08, V08 and VSb (Fig. 6a–c, respectively). The experiments were carried out in an integral reactor varying the space–time and keeping constant the feed composition and the temperature. The shape of the curves representing styrene selectivity shows that styrene is a primary product in a consecutive transformation to benzaldehyde. Note that while ethylbenzene conversion increases, the styrene selectivity decreases and benzaldehyde selectivity increases to reach a maximum. The maximum in benzaldehyde selectivity (Fig. 6b) indicates that this product is an intermediate in the reaction scheme, which produces benzoic acid. Finally, selectivity to benzoic acid decreases (Fig. 6a and c) while ethylbenzene conversion increases indicating that benzoic acid is consumed to produce carbon oxides (CO and CO_2). Since benzoic acid is the main product for all the catalysts studied, it is not possible to dismiss a direct route of its formation from ethylbenzene. Selectivity to carbon oxides is represented in Fig. 6 as CO_x selectivity where $S_{CO_x} = S_{CO} + S_{CO_2}$. It can be observed that carbon oxides selectivity curves show the behaviour of a final product in a serial reaction scheme, because they increase with the increasing of ethylbenzene conversion Therefore, the reaction scheme proposed is the following:

$$\text{ethylbenzene} \rightarrow \text{styrene} \rightarrow \text{benzaldehyde} \rightarrow \text{benzoic acid} \rightarrow CO + CO_2$$

Nevertheless, it is not possible to dismiss a direct route of total oxidation from each hydrocarbons route.

In Fig. 7, selectivity to styrene at the same ethylbenzene conversion (15%) is plotted for the three solids. It is clear from the figure that V08 has a better performance in the dehydrogenation reaction than the other two catalysts. Our theoretical studies about the partial oxidation of toluene using V–Sb mixed oxides as catalysts have shown that Sb sites are involved in the dehydrogenation step of the hydrocarbon molecule [5]. Likewise, our XPS results [1,2] have shown that V08 catalyst have a higher Sb/V surface ratio (2.2) than VSb (1.7) and Sb08 (1.6). Therefore, results reported in Fig. 7 reinforce our theoretical conclusion that Sb sites are responsible for dehydrogenation reactions.

Selectivity to partial oxidation products (benzoic acid and benzaldehyde) at the same ethylbenzene conversion (25%) is represented in Fig. 8, for the three samples. The results indicate that Sb08 has the higher selectivity to partial oxidation, while V08 has the lower one. The same results were obtained in the partial oxidation of toluene with the same catalysts [2]. This behaviour is related to the redox properties of the solids. It is well known that a good catalyst

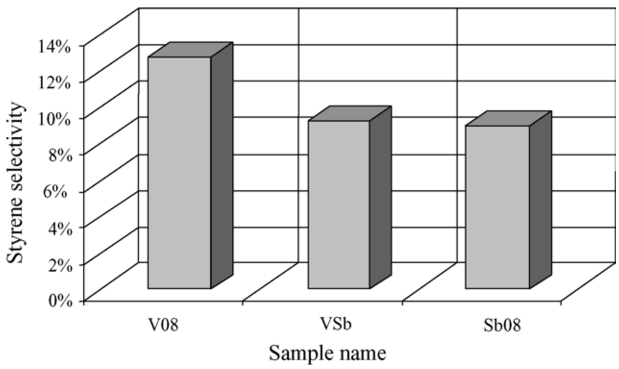

Fig. 7. Styrene selectivity for the different samples at ethylbenzene conversion = 15%.

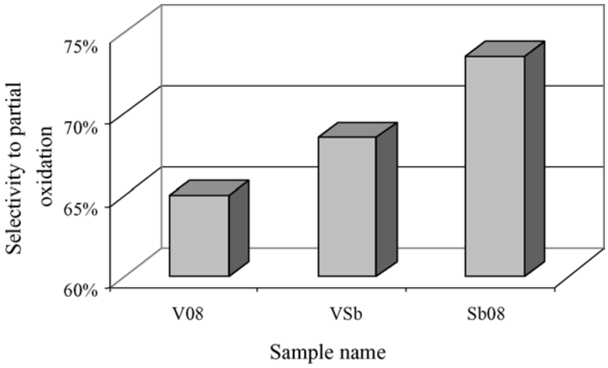

Fig. 8. Selectivity to partial oxidation products for different samples at ethybenzene conversion = 25%.

for partial oxidation must have two redox couples with different reduction potentials and efficient electron transfer between them. The separation of the reduction temperature determined by TPR experiments is related to the difference in the reduction potentials of the redox couples. Comparing Figs. 1 and 8, it can be observed that there is a direct relationship between the selectivity to partial oxidation and the separation of the reduction temperatures of both peaks of the TPR profile: the larger separation, the higher partial oxidation selectivity. In conclusion, these results confirm those obtained in partial oxidation of toluene employing the same catalysts and validate our previous interpretation [1,2,12].

Special considerations could be taken about CO and CO_2 formation. In Fig. 9, selectivity to total oxidation products, for both toluene and ethylbenzene oxidations, at the same hydrocarbon conversion and with sample Sb08 as catalysts, are plotted. It can be noticed the drastic decrease in formation of total oxidation products when ethylbenzene is the reactant. This behaviour can be attributed to formation, in the reaction mechanism of ethylbenzene oxidation, of a stable dehydrogenated intermediate, the styrene. The same phenomenon was reported in Refs. [15,16]. The styrene is preferentially adsorbed over Lewis acid sites through its double C–C bond. The oxygen is also chemisorbed on Lewis acid sites. Then, it is reasonable to suppose that the interaction of the olefinic double bond with the Lewis acid sites inhibits the oxygen adsorption, and reduces the oxygen availability on the surface. As a consequence, a drastic reduction on selectivity to carbon oxides is observed. It is necessary to indicate that the same behaviour was observed for all the samples.

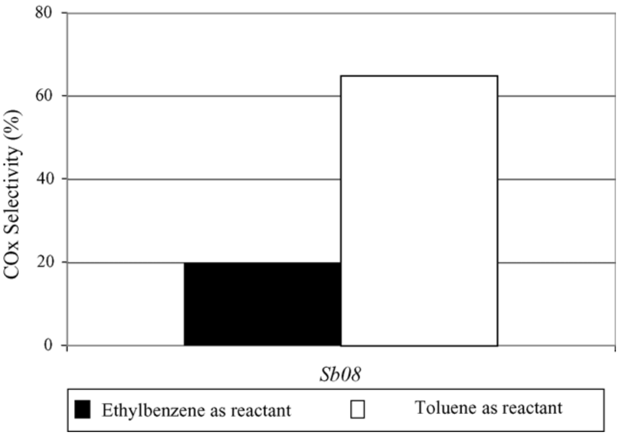

Fig. 9. Selectivity to total oxidation products for ethylbenzene and toluene as reactans. Sample Sb08; conversion = 25%.

4. Conclusions

The catalytic behaviour of vanadium antimonate oxides, partially substituted with titanium, in the ODH of ethylbenzene has been studied.

A serial reaction scheme that describes the product distribution has been proposed. Styrene was proposed as the primary product, while benzaldehyde as intermediate and total oxidation products as final products. Nevertheless, it was not possible to dismiss a possible parallel route to obtain carbon oxides from direct oxidation of hydrocarbons.

There was no evidence of formation of carbonaceous species with co-catalytic role on the catalyst surface.

In the same operating conditions, higher selectivity to carbon oxides was obtained in toluene oxidation than in ethylbenzene reaction. This observation is associated with surface modifications produced by the competitive adsorption phenomena. The adsorption of styrene in the ODH of ethylbenzene inhibits the oxygen chemisorption at surface Lewis active sites. Thus, the formation of electrophilic oxygen, responsible for the total oxidation of hydrocarbon molecule, is controlled, and the selectivity to total oxidation products decreases. Besides, due to the adsorption of styrene, a change in the acid–base properties of the catalyst surface could be expected. In fact, benzoic acid was the main partial oxidation product in ethylbenzene oxidation reaction while benzaldehyde was the unique partial oxidation product in toluene oxidation.

By comparing the results obtained in the ODH of ethylbenzene and the oxidation of toluene it was possible to confirm that the reaction rate is independent of the hydrocarbon used as reactant, and is related with V/Sb bulk ratio, but pointing out that the reoxidation of the catalyst controls the overall reaction rate.

Likewise, a relation between the dehydrogenation function and the Sb/V catalyst surface ratio is proposed. The catalyst with higher Sb/V ratio on surface presents higher selectivity to styrene, in agreement with our previous theoretical results, which assigns to Sb sites the H-abstraction function.

Finally, our previous assignment about the relationship between selectivity to partial oxidation products and the redox properties of the solids has been validated because the same relation was observed in the ODH of ethylbenzene on the same catalysts.

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