Effect of Fe doped over V–Sb oxide catalyst in toluene selective oxidation

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Abstract

Mixed oxides $Fe_xV_{1-x}SbO_4$ with $x = 0$–1.0 were prepared by slurry method and characterized by X-ray diffraction (XRD), Mössbauer spectroscopy, and temperature-programmed reduction (TPR). The samples with $x = 0$, 0.4 and 1.0 were evaluated as catalyst in vapor phase toluene partial oxidation reaction. It was found by XRD that Fe, as doping, was introduced in the rutile structure of $VSbO_4$. The BET surface area of partially substituted solid with $x = 0.4$ was higher than those obtained for $VSbO_4$ and $FeSbO_4$ samples. It was shown that V is responsible of the hydrocarbon molecule activation. The catalyst with Fe $x = 0.4$ presented lower specific rate reaction and lower selectivity to total oxidation products than undoped solid ($VSbO_4$), which it would be related to a partial replace of V by Fe in the V–O–V chains.

In conclusion, the solid activity and selectivity to total oxidation decrease due to a higher isolation of V sites, when V^{3+} is substituted by Fe^{3+} in the rutile structure.

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1. Introduction

In the last years, the researches related to the study of V–Sb mixed oxides as solid catalysts in selective oxidation processes have increased significantly.

$VSbO_4$ oxide is being studied in order to analyze its behavior as catalyst in selective oxidation reactions. This oxide results particularly adequate for selective oxidation of alkanes, which means that it is possible to replace more expensive raw material, as alkenes by the corresponding alkane, in industrial processes in order to produce key intermediates in organic synthesis.

The object of this study is to develop a solid catalyst highly selective to partial products oxidation and slightly selective to total oxidation products ($CO + CO_2$). In this sense, it is known that vanadium antimonate presents a rutile structure with the following composition $V_{0.92}Sb_{0.92}\square_{0.08}O_4$ where $\square$ indicates cationic vacancies [1]. The activity and selectivity to partial oxidation products are strongly associated with V^{4+}/V^{3+} and Sb^{5+}/Sb^{3+} ratios. Previous studies [1,2] employing vanadium antimonate partially substituted by titanium as catalyst led to postulate that activity and selectivity are determined by V^{4+}/Sb^{5+} ratio in the unit cell. These studies concluded that V^{4+} atoms are involved in the incorporation of gaseous oxygen as lattice oxygen and hold the Sb sites in an oxidation state (Sb^{5+}) high enough to insert the lattice oxygen in to hydrocarbon molecule. Besides, we have found that selectivity to total oxidation products (CO and CO_2) is related to V–O–V chains responsible of the O electrophilic adsorption and therefore of total oxidation processes.

In conclusion, when Sb was partially substituted by Ti ($VSb_{1-x}Ti_xO_4$), a higher selectivity to partial oxidation products was obtained. On contrary, the partial substitution of V by Ti in the rutile structure reduced the number of V–O–V chains that were replaced by the corresponding V–O–Ti, and derived in lower selectivity to total oxidation products. Therefore, the challenge is to find a cation as doping of $VSbO_4$ oxide, which partially replaces to V in the rutile cell, in

order to decrease the formation of CO and CO_2 and at the same time leads to a higher electron transfer between V^{4+} and Sb^{5+}.

In this sense, Fe appears as possible cation doping since that $FeSbO_4$ crystallizes in the same type of structure as $VSbO_4$ and Fe^{3+} has the same cationic radius as V^{3+}.

The aim of this work is to analyze the redox and structural properties of the solid oxides with nominal compositions $Fe_xV_{1-x}SbO_4$ with $x = 0$–1.0, and to determine the effect of Fe as doping on $VSbO_4$ catalyst in vapor phase toluene selective oxidation.

2. Experimental

2.1. Catalyst preparation

The $Fe_xV_{1-x}SbO_4$ catalysts have been prepared by slurry method using two different procedures, depending on the iron content. Samples with $x < 0.6$ have been prepared according to a procedure described for $FeSbO_4$ [3]. Sb_2O_3 oxide is added under stirring to $(NH_4)VO_3$ and $Fe(NO_3)_3 \cdot 9H_2O$ solution and heated under reflux during 8 h. The solution was then evaporated and the resulting slurry dried at 373 K before calcination at 623 K for 4 h and 923 K for 6 h. During preparation of solid with $x > 0.6$, $Fe(NO_3)_3 \cdot 9H_2O$ was heated to 353 K and Sb_2O_3 and $(NH_4)VO_3$ were then added under stirring. The solution was neutralized using NH_3, filtered and dried 373 K for 24 h. The resulting solid was then calcined in air at 773 K for 16 h and at 1173 K for 3 h, respectively [4]. The catalysts are identified according to their relative vanadium and iron contents.

2.2. Characterization

The solids are characterized by sorptometry, X-ray diffraction (XRD), temperature-programmed reduction (TPR) and Fe Mössbauer spectroscopy.

Sorptometry experiments were performed with nitrogen at 77 K in a Micromeritics Gemini 2360 equipment in order to determine the BET-specific surface area of the solids.

The X-ray diffraction patterns were collected with a Philips PW3710 powder diffractometer equipped with graphite mono-chromatic and Cu Kα radiation, in a Bragg–Brentano geometric. Data were collected with 2θ step of $0.020°$ and $0.24°$/min. The data sets were refined using Rietveld analysis method.

Fe Mössbauer spectroscopy was performed at 298 K, $^{57}Co/Rh$ was used as a radiation source and a constant acceleration drive.

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 temperature ramp-rate of 10 °C/min. The operating conditions were chosen from those recommended by Monti and Baiker [5]. The profile obtained permit to get information about redox behavior of the mixed oxide.

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 toluene/air molar ratio in the feed was controlled by adjusting the saturator temperature. The reaction temperature was measured with a sliding thermo-couple placed inside the bed. Since the oxidation reactions are highly exothermal, 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. A multicolumn HP 6890, equipped with thermal conductivity (TCD) and flame ionization (FID) detectors was used. Organic reactant and selective oxidation products were separated on an HP INNOWAX 30 m/320 μm/0.25 μm polyethyleneglycol column and sensed by a FID detector. Total oxidation products were analyzed by the TCD detector using CTR1 6 ft × 1/4 in. column:

- Selectivities (S) were calculated as: mole of products × no. of C atoms in the compound/mole of toluene converted × 7.
- Conversion (x) of toluene was calculated as: (mole of toluene in the feed − mole of toluene in the effluent)/mole of toluene in the feed.

In order to insure that the kinetic experiments to give meaningful results, preliminary catalytic tests were carried out at different particle diameter and total gas flow, and at the same residence time. Some of them were performed without catalysts in order to verify the absence of the thermal oxidation. These tests showed a negligible contribution of homogeneous oxidation to total oxidation and the absence of internal and external diffusion limitations, for a particle diameter below 120 μm and total gas flow equal or higher than 100 ml min^{-1}, respectively. The catalyst was stable during a typical run period of 12 h.

The reactor was operated in steady-state conditions. The catalytic tests were performed under the following conditions: catalyst mass: 40–240 mg; temperature: 523–713 K; total feed rate: 400 ml/min; toluene molar fraction: 0.008; oxygen molar fraction: 0.18 and nitrogen balance; particle diameter <120 μm.
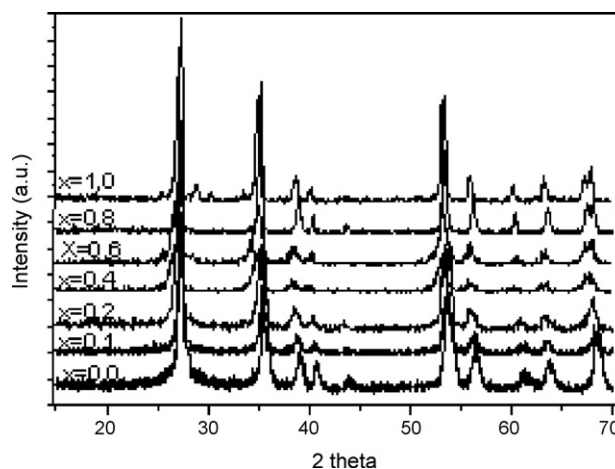

Fig. 1. XRD patterns of $Fe_xV_{1-x}SbO_4$ samples with $x = 0$; 0.1; 0.2; 0.4; 0.6; 0.8; 1.0.

Table 1
Cell parameters of the tetragonal rutile phase calculated for $Fe_xV_{1-x}SbO_4$ samples

x	a (Å)	c (Å)
0	4.6235	3.0255
0.1	4.6254	3.0351
0.2	4.6295	3.0399
0.4	4.6297	3.0559
0.6	4.6235	3.0554
0.8	4.6287	3.0721
1.0	4.6368	3.0715

3. Results

The XRD patterns of solids are presented in Fig. 1. The solids $Fe_xV_{1-x}SbO_4$ with $x = 0$–0.8, present a single phase. For the sample with $x = 1.0$ ($FeSbO_4$) three phases are detected, two of them are minority phases, one related to antimony oxide formation (8%) and the other one related to hematite formation (Fe_2O_3) (5%). All the solids show a well-crystallized rutile-type phase, which represents the single phase for samples with $x = 0$–0.8 and the larger phase for sample with $x = 1.0$. The a and c parameters of the simple tetragonal unit cell were calculated. It can be observed in Table 1 that c parameter increased progressively with the vanadium content indicating the formation of a solid solution.

[57]Fe Mössbauer spectroscopy was used to characterize the average state of iron in the compounds. The spectra of the samples were fitted with one ferric doublet (Fig. 2). This doublet is caused by paramagnetic Fe^{3+} ions, with high spin in octahedral coordination (Isomer shift, IS: 0.38).

The high value of quadrupolar splitting (QS) accounts (0.71) should arise from a distortion of the octahedral formed with the nearest oxygen neighbors. In order to adjust the spectra of $FeSbO_4$, besides the doublet mentioned (90%), a sextet corresponding to hematite (10%) (IS: 0.37, QS: 0.21), in concordance with the XRD results, was considered.

TPR profiles of the samples are shown in Fig. 3. For $x = 1.0$ ($FeSbO_4$) is observed the presence of an only pick with a
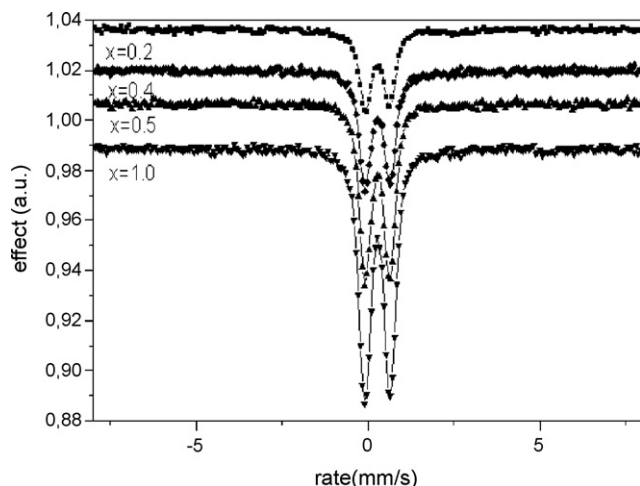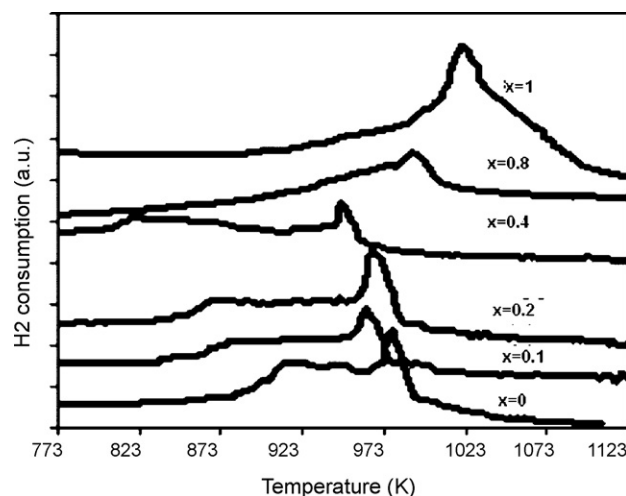

Fig. 3. Temperature-programmed reduction profiles of $Fe_xV_{1-x}SbO_4$ samples.

maximum at 750 °C. This signal corresponds to Sb reduction in the rutile phase [1]. With the progressive increase of vanadium content the formation of a shoulder on Sb pick and the appearance of a second pick at lower reduction temperature is observed. Therefore, it is possible to suggest that the signals at higher temperature correspond to reduction of Sb^{3+} and Sb^{5+}, and the pick at lower temperature correspond to $V^{4+/3+}$ reduction. The analysis of the TPR profiles indicates that an efficient redox system for electron transfer would be achieved for the sample with $x = 0.4$, since the temperature difference between the first and the second pick is the highest [2]. Thus, this oxide could be a good catalyst for partial oxidation of toluene. Therefore we will carry out the kinetic evaluations using $Fe_xV_{1-x}SbO_4$ as catalyst with $x = 0$; 1.0 and 0.4.

BET surface area (S_g) measurements of the samples with $x = 0$; 0.4 and 1.0 are shown in Table 2. It can be appreciated that the sample $Fe_{0.4}V_{0.6}SbO_4$ has the highest BET surface area, in agreement with Roussel et al. [6]. It could be proposed that Fe acts as separator avoiding the sintering during the calcination processes.

The catalyst was stable during toluene partial oxidation reaction and the products formed were benzaldehyde, benzoic acid, carbon monoxide and carbon dioxide. The reaction rate (r_m mol/(min g(cat))) of the samples with $x = 0$; 0.4 and 1.0 at different temperatures are shown in Fig. 4. The sample with $x = 1.0$ ($FeSbO_4$) presented the lowest reaction rate at all temperatures analyzed. Then, it can be concluded that vanadium is essential for catalytic activity of VSb oxides. This conclusion is in agreement with the results obtained by other authors [7–9] who have postulated that $FeSbO_4$ was not a good catalyst for oxidation. On the other hand, the highest

Fig. 2. Mösbauer spectra of $Fe_xV_{1-x}SbO_4$ samples with $x = 0.1$; 0.2; 0.4; 0.5; 1.0.

Table 2
BET surface area of $Fe_xV_{1-x}SbO_4$ samples with $x = 0$; 0.4; 1.0
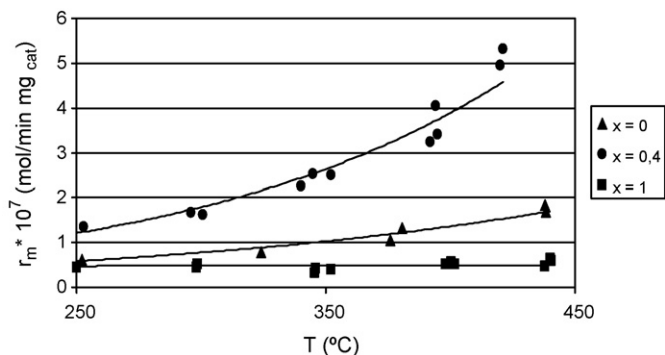
x	S_g (m²/g)
0	3.0
0.4	21.0
1.0	10.0

Fig. 4. Effect of temperature on reaction rate of $Fe_xV_{1-x}SbO_4$ samples with $x = 0$; 0.4; 1.0.

reaction rate was obtained by the sample with $x = 0.4$ ($Fe_{0.4}V_{0.6}SbO_4$). Since the solids presented different surface areas, the specific reaction rates ($r_s = r_m/S_g$) were estimated for comparison. It can be observed (Fig. 5) that the highest specific activity was obtained with the sample with $x = 0$ ($VSbO_4$).

The effect of Fe doping on product selectivities of samples with $x = 0$ and 0.4 at 653 K were analyzed. The results were determined at different residence times in order to compare selectivities at the same conversion. The results are shown in Figs. 6 and 7.

Comparing the product selectivity obtained for both catalysts at the same conversion level it is possible to appreciate there is no significant difference between them.
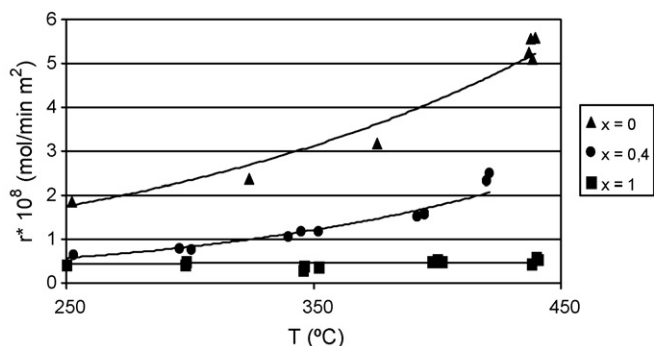

Fig. 5. Effect of temperature on specific reaction rate of $Fe_xV_{1-x}SbO_4$ samples with $x = 0$; 0.4; 1.0.
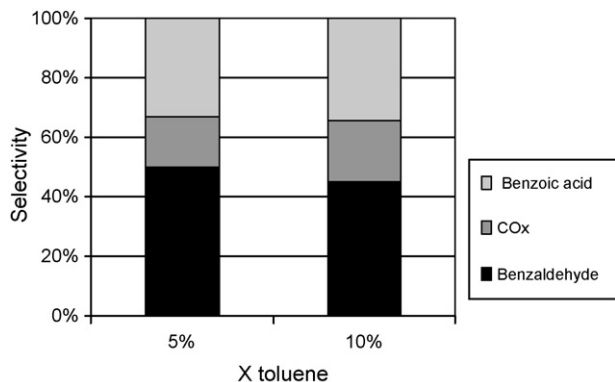

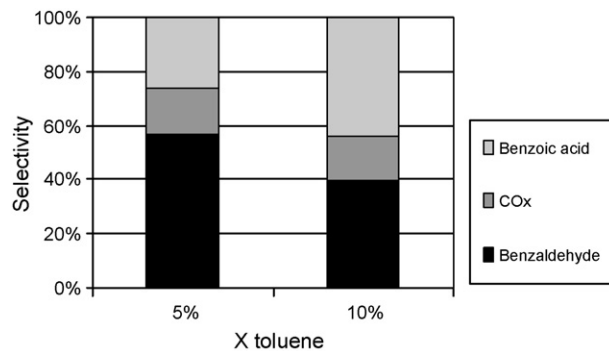Fig. 6. Product distribution of $VSbO_4$ catalyst at different toluene conversions (5 and 10%).

Fig. 7. Product distribution of $Fe_{0.4}V_{0.6}SbO_4$ catalyst at different toluene conversions (5 and 10%).

Nevertheless, for the catalyst with $x = 0$ (Fig. 6) when conversion increases, the selectivity to benzaldehyde decreases and total oxidation selectivity increases. On the other hand, for the catalyst with $x = 0.4$ (Fig. 7) when conversion increases, benzaldehyde selectivity decreases and benzoic selectivity increases while the selectivity to total oxidation products ($CO + CO_2$) remains constant. Evidently, Fe as doping does not promote the total oxidation of partially oxidized intermediates. This behavior would be related with the site isolation theory [10], due to the partial substitution of V by Fe in chains V–O–V, which are responsible of total oxidation.

4. Conclusions

$Fe_xV_{1-x}SbO_4$ mixed oxides were prepared by slurry method and characterized by sorptometry, XRD, TPR and Fe Mössbauer spectroscopy. Their catalytic behavior was determined in toluene selective oxidation. It is found that Fe^{3+} as doping is introduced in the rutile structure of $VSbO_4$. The specific surface area of the partial substituted solid with $x = 0.4$ was higher than those obtained for the samples with $x = 0$ and 1.0. It is known that V acts as activator of hydrocarbon molecule [11]. This is in concordance with the lower activity obtained using $FeSbO_4$ as catalyst.

In conclusion, if V^{3+} is substituted by Fe^{3+} in the rutile structure, the solid is becoming to a lower activity and selectivity to total oxidation due to a higher isolation of V sites.

Finally, the doped with Fe ($Fe_{0.4}V_{0.6}SbO_4$) does not seem to modify the selectivity to partial oxidation products. As it was reported previously [1,2], the selectivity to partial oxidation would be related to an efficient electron transfer between V and Sb cations, then we can suggest that, at least, the presence of Fe does not affect this redox mechanism.

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