

Catalytic activity and selectivity of perovskites $\text{La}_{1-x}\text{Sr}_x\text{V}_{1-x}^{3+}\text{V}_x^{4+}\text{O}_3$ for the transformation of isopropanol

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Received 6 April 1995; accepted 15 May 1995

Abstract

The catalytic decomposition of isopropyl-alcohol (IPA) was studied over the perovskite series $\text{La}_{1-x}\text{Sr}_x\text{V}_{1-x}^{3+}\text{V}_x^{4+}\text{O}_3$ ($x=0.0, 0.05, 0.1, 0.2, 0.4, 0.6, 0.8, 0.9, 0.95, 1.0$) in the range 200–300°C. Catalyst characterization by XRD shows that gradual substitution of La^{3+} by Sr^{2+} transforms the LaVO_3 structure to SrVO_3 , both of cubic symmetry. ESR spectra at 13 K shows that the V^{4+} (d^1) centers are localized in the form of vanadyl groups up to $x \approx 0.6$, while thereafter they become delocalized. The catalytic transformation of IPA over these solids shows that the products obtained are propene and acetone. The selectivity of the reaction for $x=0.0$ is ca. 15% for acetone (85% propene) and increases linearly with the substitution of La by Sr reaching at $x=1.0$ the value of 40% (60% propene). The total reaction rate was maximum at $x=0.0$ and drops up to $x=0.2$, thereafter remaining almost steady. The apparent activation energies calculated for the total conversion of IPA (E_{tot}) according to the first order kinetics are clustered around 120 kJ/mol. These values are almost similar to those found for the acetone formation (E_{acet}) while those estimated for the propene formation (E_{prop}) are lower by an amount of 10–15 kJ/mol on average. A common compensation effect observed for the production of propene and acetone is explained by the variation of the heats of adsorption of the product. The reaction route seems negligibly influenced by electronic effects of the solids and it is mainly controlled by the acid/base function of the solid surface.

Keywords: Activity; Selectivity; Perovskites; $\text{La}_{1-x}\text{Sr}_x\text{V}_{1-x}^{3+}\text{V}_x^{4+}\text{O}_3$; Isopropanol

1. Introduction

Perovskites containing vanadium have attracted little attention relative to their catalytic activity over the past years. A computer search in the various chemical

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data banks using the keywords 'perovskite' and 'vanadium' from 1967 to 1993 produced 23 literature entries. Of them, only one referred to catalytic studies [1], the rest dealing with structural or physical studies of such perovskites, mainly in relation to their conductive and magnetic properties. An additional literature search in more traditional ways revealed that the only vanadium perovskite studied as a catalyst was actually SrVO_3 which was tested for methanol and benzene oxidation [2] as well as electrode material in anodic oxidation [3]. Another vanadium perovskite also prepared is LaVO_3 [4]. Finally, similar binary oxides of vanadium have been proposed as catalysts for the vapour-phase catalytic dehydrogenation of paraffins [5].

The extensive research on vanadium perovskites by solid state physicists or chemists, especially on solids like SrVO_3 , Sr_2VO_4 and relative structures [6–10], is justified by the hope that such solids, which are layered compounds and contain the $d^1(\text{V}^{4+})$ cations instead of $d^9(\text{Cu}^{2+})$ ones, might give rise to high temperature superconductivity as other perovskites containing copper do [11]. The interest on such perovskite superconducting solids in relation to their catalytic action has been extensive and the subject has been reviewed recently [12], but although vanadium perovskites do not appear often in the literature, there might exist important reasons for testing them. Namely, supported and unsupported vanadia is a first choice catalyst for the selective mild oxidation of aromatics [13–15] but the stabilization of the oxidation state of this element poses a serious problem. Indeed there are as many as seven oxide phases between V_2O_3 and V_2O_5 [16] so a way of stabilizing such phases can be in the form of oxyanions as those in perovskites SrVO_3 and/or LaVO_3 . Both those perovskites have cubic structures with $a = 3.84 \text{ \AA}$ and 3.99 \AA , respectively. So we decided to check to what extent those solids can form substitutional series of the form $\text{La}_{1-x}\text{Sr}_x\text{V}_1^{3+}\text{V}_x^{4+}\text{O}_3$ and how this substitution affects their surface and catalytic properties. As a test reaction we have chosen at this stage the simple conversion of isopropyl-alcohol (IPA) since the existence of oxygen in the reaction mixture often transforms the vanadium to higher oxidation states in structures like $\text{Sr}_2\text{V}_2\text{O}_7/\text{Sr}_3\text{V}_2\text{O}_8$ and LaVO_4 [2,17]. We notice that the decomposition of IPA is often considered a model reaction for estimating the acid or basic character of the surface. In the literature there does not appear to be any reference to decomposition of IPA over $\text{LaVO}_3/\text{SrVO}_3$ solids, the only relevant work referring to dehydration activity of LiV_2O_5 materials [18]. The questions addressed in this study include the following. How does the substitution of La by Sr affect the catalytic dehydration and/or dehydrogenation of IPA? Is the final effect dependant only on the acid/base function of the surface or does the gradual transformation of $\text{V}^{3+} (d^2)$ cation into $\text{V}^{4+} (d^1)$ also affect the reaction products?

2. Experimental

2.1. Preparation of $\text{La}_{1-x}\text{Sr}_x\text{VO}_3$ solids

The perovskite solids $\text{La}_{1-x}\text{Sr}_x\text{VO}_3$ ($x = 0.0, 0.05, 0.1, 0.2, 0.4, 0.6, 0.8, 0.9, 0.95, 1.0$) were prepared in ca. 3 g quantities as follows. The calculated amounts

Table 1

The solids $\text{La}_{1-x}\text{Sr}_x\text{VO}_3$, the apparent activation energies for the indicated processes and the average selectivity towards acetone

Sample	$E_{a(\text{total})}$ (kJ/mol)	$E_{a(\text{acetone})}$ (kJ/mol)	$E_{a(\text{propene})}$ (kJ/mol)	% S_{acetone}
LaVO_3	112.2	121.5	104.8	9.9
$\text{La}_{0.95}\text{Sr}_{0.05}\text{VO}_3$	138.0	144.7	126.0	18.3
$\text{La}_{0.9}\text{Sr}_{0.1}\text{VO}_3$	127.2	129.0	114.4	19.4
$\text{La}_{0.8}\text{Sr}_{0.2}\text{VO}_3$	117.2		106.8	24.1
$\text{La}_{0.6}\text{Sr}_{0.4}\text{VO}_3$	121.4	163.9	131.4	27.4
$\text{La}_{0.4}\text{Sr}_{0.6}\text{VO}_3$	120.6	121.2	115.2	32.7
$\text{La}_{0.2}\text{Sr}_{0.8}\text{VO}_3$	107.2	109.0	95.6	33.0
$\text{La}_{0.1}\text{Sr}_{0.9}\text{VO}_3$	113.9	118.6	109.0	36.4
$\text{La}_{0.05}\text{Sr}_{0.95}\text{VO}_3$	119.7	116.8	106.6	37.7
SrVO_3	103.1	106.0	95.9	39.2

of V_2O_5 in water suspension (ca. 50 ml) were reduced by 2 drops of hydrazine. A black slurry was formed after slightly heating for a few minutes in a water bath. Then the calculated amounts of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Sr}(\text{NO}_3)_2$ were dissolved in the parent solution. Finally an amount of citric acid was added to it, equivalent to the moles of metals dissolved. This method is usually known as the citric route [19]. After the addition of citric acid and slight heating the solution turned a clear bright blue colour. The mixture was then dried very carefully at 100°C in a water bath and fired gradually under air flow up to 900°C where it remained for 2 h. In this way the nitrates and the organic part of the precursor were decomposed. The intermediate product obtained was then ground in an agate mortar and fired again at 900°C in a tubular furnace under a flow of H_2 (10 ml/min for 6 h with an intermediate grinding). The solids obtained are indicated in Table 1.

The specific surface areas of the solids measured by nitrogen adsorption at 77 K were rather low ($1\text{--}2\text{ m}^2\text{ g}^{-1}$) so they were not taken into account in the estimation of the catalytic results discussed in the next section.

2.2. Thermogravimetry

A small amount of the precursors, after drying at 100°C , were tested in a thermobalance to examine the mode of their decomposition from $100\text{--}800^\circ\text{C}$. The instrument used was a model TRDA₃-H of the Chyo Balance Corporation connected to a PC and able to detect the T (temperature), TG (thermal gravimetry), DTG (differential thermal gravimetry) and DTA (differential thermal analysis) signals. The atmosphere in the thermobalance was controlled by a flow of either air and/or N_2 at 20 ml/min and the temperature increment was set at $5^\circ\text{C}/\text{min}$. The results obtained are shown in Fig. 1.

2.3. XRD

The prepared solids were examined as to their structure by X-ray diffraction. The powder method was used in a Siemens system with $\text{CuK}\alpha$ radiation ($\lambda = 1.5418\text{ \AA}$). The results are shown in Fig. 2.

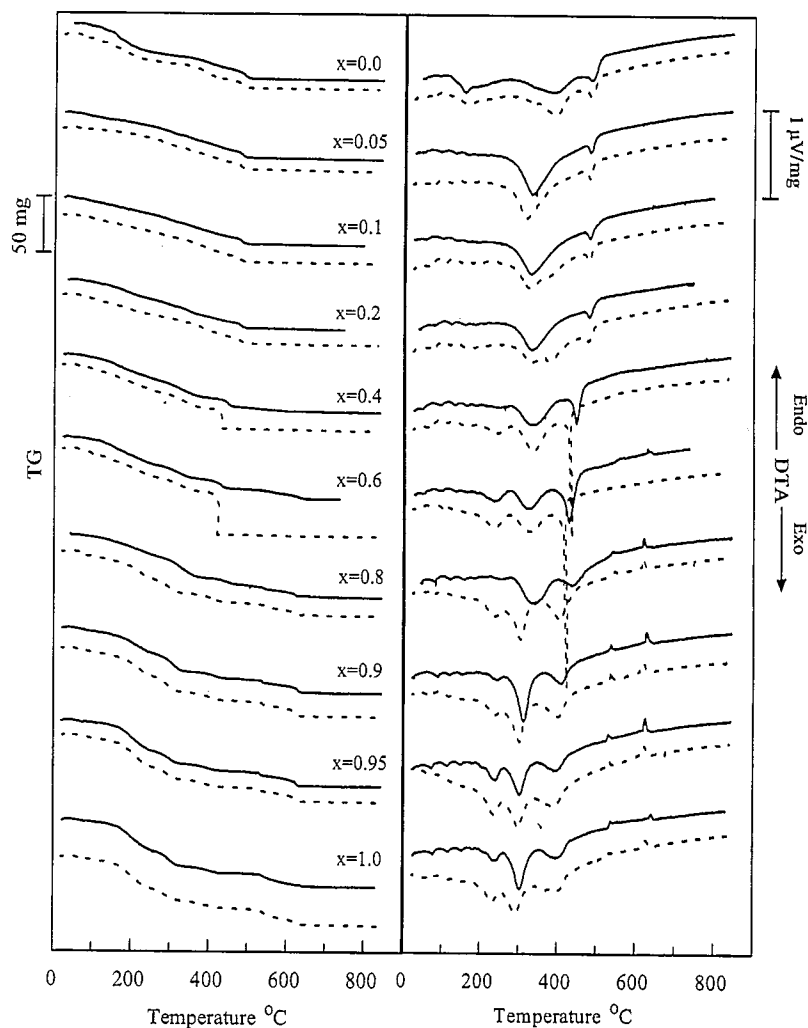


Fig. 1. TG and DTA signals of the decomposition of precursors in a flow of N_2 (solid line) and air (dotted line); x is the corresponding value in $La_{1-x}Sr_xVO_3$.

2.4. ESR Spectra

The ESR spectra of the prepared solids were checked at 4, 14 and 18 K in a Bruker ER 200 D instrument equipped with a liquid helium facility. The spectra obtained at 13 K are shown in Fig. 3. The spectra at 4 and 18 K were similar to those indicated in Fig. 3.

2.5. Catalytic experiments

The catalytic decomposition of IPA took place in a bench-scale flow microreactor similar to that described in [20,21]. Briefly the reactor consisted of a silica tube, 1 cm in diameter with a perforated glass bed onto which 0.5 g of the catalyst was

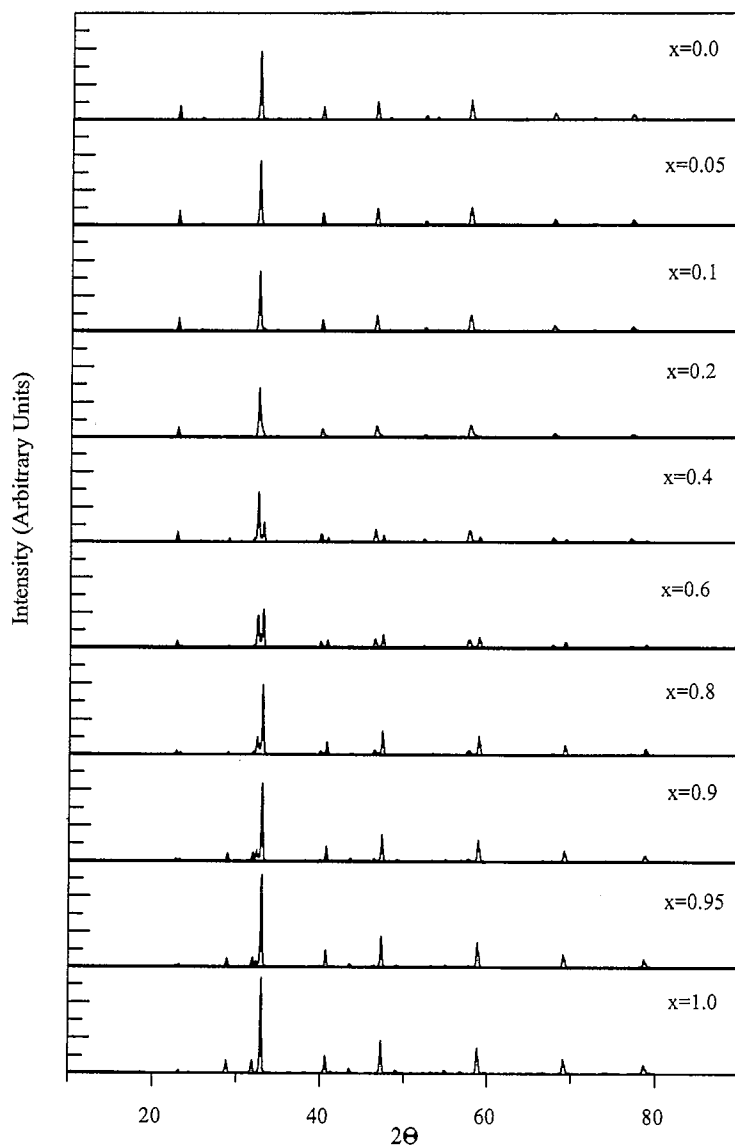


Fig. 2. XRD patterns of $\text{La}_{1-x}\text{Sr}_x\text{VO}_3$ solids.

placed. The system was heated with a tubular furnace with a control system to within $\pm 2^\circ\text{C}$. Analyses of reactants and products were carried out by sampling 1 cm^3 of the gases in a Shimadzu GC-15A gas Chromatograph equipped with a thermal conductivity detector and connected to Chromatopac C-R6A integrator. The column used for analysis was a 2 m stainless steel 0.125 in. tube (1/8") containing 10% Carbovax 20M-Chrom WR/N 0–100 mesh. Helium was used as the carrier gas in the gas chromatograph. Helium was bubbled through a bottle ($40 \pm 2\text{ ml/min}$) containing the IPA, which was then passed through the reactor. Under the experimental conditions, the partial pressure of IPA was 32.8 mmHg. Measurements were taken randomly between 200–300°C at 10°C intervals. Before

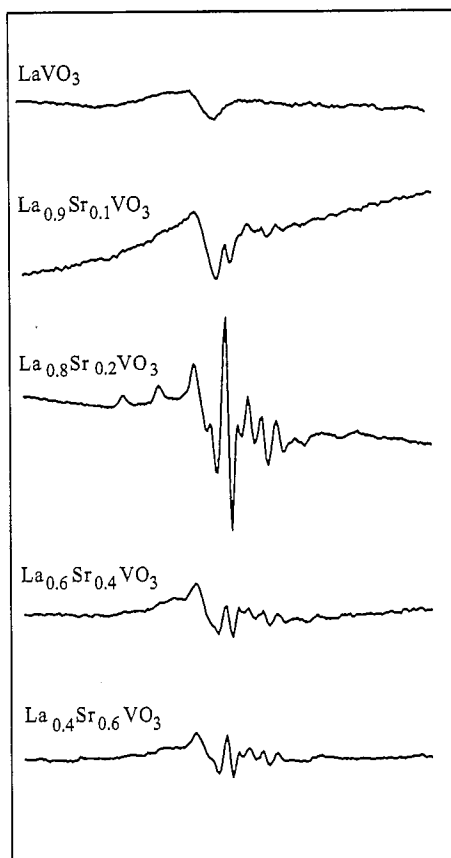


Fig. 3. ESR spectra of the solids $\text{La}_{1-x}\text{Sr}_x\text{VO}_3$ at 13 K. For $x > 0.6$ no spectra was detectable even at 4 K.

any measurements were made the reaction was allowed to run for 30 min. No signs of catalyst 'die-off' were observed during the the experiments. From the percent-
ance degree of conversion the reaction rate per unit catalyst mass was calculated and the results are shown in Fig. 4.

3. Results and discussion

3.1. The thermogravimetric experiment

From the experimental TG and DTA results referred to the thermal decomposition of precursors in a flow of either N_2 or air (Fig. 1) it can be seen that their weight stabilized above 700°C . Therefore, the final firing temperature was set to 900°C , since at these temperatures the perovskite phase is usually formed in the so-called citrate method employed here [19]. The DTA results in this figure show that the precursor of LaVO_3 solid is decomposed exothermically, the main thermal effects being detected around 400 and 500°C . Those exothermic-peaks, which should be due to the decomposition of nitrate and the burning of organic part of the precursor,

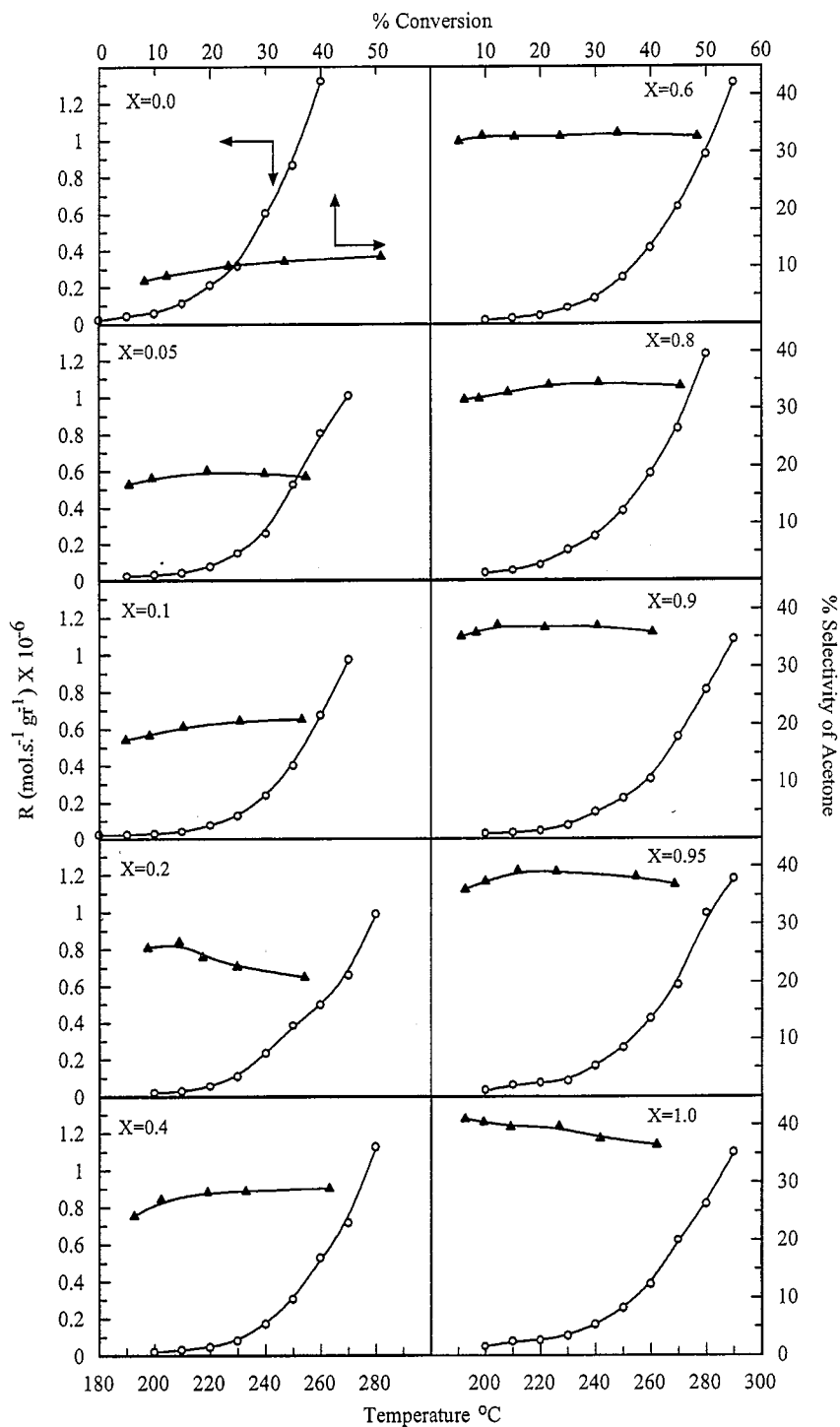


Fig. 4. Reaction rate (mol s⁻¹ g⁻¹) for the total conversion of IPA on $\text{La}_{1-x}\text{Sr}_x\text{VO}_3$ solids versus temperature (○) and selectivity for the production of acetone (▲) versus the conversion.

moved gradually but steadily to lower values by the gradual substitution of La by Sr and reach around 300 and 400°C, respectively, by the total substitution of La by Sr in the mixture. Both Sr^{2+} and La^{3+} ions are not considered as possessing catalytic ability for the decomposition of nitrates [22,23]. This is because they are not able to exist in at least two different oxidation states suffering oxidation–reduction cycles and thus forcing the reduction of nitrates. If so, the lowering of the decomposition temperature of the precursors should be due to the differentiation of oxidation state of vanadium. In other words the higher amount of $\text{V}^{4+}(\text{d}^1)$ in the rich in Sr precursors seems to be more active than the $\text{V}^{3+}(\text{d}^2)$ ions existing in the rich in La precursors. This is strange since d^1 electronic configurations usually behave less as potential catalysts as compared to d^2 ones according to the standard crystal field theory of heterogeneous catalysis [24,25]. Nevertheless it has been proposed [26,27] that the catalytic ability of various cations for the decomposition of nitrates is related to the standard redox potential of the coupled pair $\text{M}^{+n}_{\text{reduced}}/\text{M}^{+n+1}_{\text{oxidized}}$. In our case the standard electrode potentials are $\text{V}^{4+}/\text{V}^{5+} = -1.0$ Volts and $\text{V}^{3+}/\text{V}^{4+} = -0.34$ Volts. So it may be that the higher values of $E^{\circ}_{\text{V}^{4+}/\text{V}^{5+}}$ as compared to those of $E^{\circ}_{\text{V}^{3+}/\text{V}^{4+}}$ is the reason for the easier decomposition of nitrates and/or citrate groups in the Sr^{2+} rich/ V^{4+} rich precursors.

An additional interesting effect in the DTA signals is the violence of decomposition observed in the samples with $x=0.4$ and 0.6 . This is more clear in the case of experiments with air, where a small explosion actually takes place (see Fig. 1). In this range of substitution the solids $\text{La}_{1-x}\text{Sr}_x\text{VO}_3$ contain an almost equal number of V^{3+} and V^{4+} ions. So it is as though in the substitution region where the maximum density of $\text{V}^{3+}-\text{V}^{4+}$ pairs is present, the catalytic effect on the decomposition of precursor is maximized.

3.2. The XRD results

The results taken by XRD and shown in Fig. 2 show clearly the perovskite phases, LaVO_3 in the samples rich in La ($x \leq 0.2$) and SrVO_3 in the samples rich in Sr ($x \geq 0.8$). The intermediate samples with $x=0.4$ and 0.6 contain both phases. Both phases possess cubic structure with $a=3.84$ Å (LaVO_3) and $a=3.99$ Å (SrVO_3) in full agreement with the data in the literature [17]. The transformation of the LaVO_3 phase into SrVO_3 happens abruptly from $x=0.4$ to 0.6 or 0.8 . It is worth noting that exactly in this range an explosive decomposition of the precursor take place as described previously but also the d^1 ESR signal is delocalized as described next.

3.3. ESR results

The ESR signals from the solids were detected at 4, 13 and 18 K. Typical signals at $T=13$ K are shown in Fig. 3. Following closely [28–30] they were identified as being due to localized vanadyl groups. Moreover these ESR spectra are character-

istic of immobile VO^{2+} species [28–30]. The spectrum for the solid with $x=0.2$ shows the best resolution for these species. The spectrum for the solids with $x<0.2$ is not so clear due to the very low concentration of VO^{2+} species into the sample. With increasing substitution of La by Sr the ESR signal becomes more and more noisy up to $x=0.6$. Beyond that substitution it was not possible to freeze and detect the ESR signal. This phenomenon can be explained as being due to the development of a non-insulating behaviour of the solids. In other words the materials has started acting as a conductor. Trivial calculations reveal that in this range of substitution ($x=0.6$) where the ESR signal disappears the average distance between two $\text{V}^{3+}(\text{d}^1)$ centers is ca. 6.5 Å. This value is indicative of the distance where the long range interactions are effective between pairs of d^1 centers. It is worth noting that the half of this distance, which equals ca. 3.25 Å, equals 4–5 times the corresponding ionic radius of the vanadium cations.

3.4. The catalytic transformation of IPA

The conversion of isopropyl-alcohol (IPA) can proceed either to propene on acid surface sites or towards acetone on basic sites or metallic surfaces [20,31–33]. The literature on this reaction is rather extensive [34–46] the reason being that it provides a model for estimating the acid and/or basic functionality of a catalyst surface. For dehydration, which leads to propene formation, acid surface sites are required [32] via one of the following three mechanism: E_1 (Bronsted H^+ site), E_2 (acid-base pair site) or concerted $\text{E}_{1\text{CB}}$ (acid-base pair site) [38–41]. For dehydrogenation on the other hand, leading to acetone, either basic surface sites or metallic surfaces are needed [32,47] via a mechanism involving either an alkoxide intermediate [42,43] or an enolate intermediate [44]. Nevertheless a recent detailed study explored the effect of coordination of cations in LiAlO_2 solids on their basicity, and the products of IPA decomposition [33]. The authors concluded that cations in tetrahedral sites are weaker bases as compared to cations in octahedral coordination.

The results in Fig. 4 show the profiles of the total conversion rate versus temperature as well as the calculated selectivity relative to acetone (see also Table 1). From these results the rate of the total conversion as well the selectivity is drawn in Fig. 5 versus the degree of substitution x of La by Sr in $\text{La}_{1-x}\text{Sr}_x\text{VO}_3$ at typical reaction temperatures.

From Fig. 5 it can be seen that the reaction rate is higher on the solids LaVO_3 providing propene at a selectivity ca. 85% while the produced acetone is around 15%. Then from $x=0.0$ to $x=0.1$ the activity drops to almost half of its original value. Thereafter it remains almost constant at this value up to full substitution of La by Sr. A slight increase of activity at $x=0.8$ appears out of this trend. At the same time the selectivity for propene decreases and at $x=1.0$ (SrVO_3) reaches ca. 50–55% while acetone is around 45–50%. The selectivity for the production of propene (or the acetone) appears to be strictly linearly related to the substitution

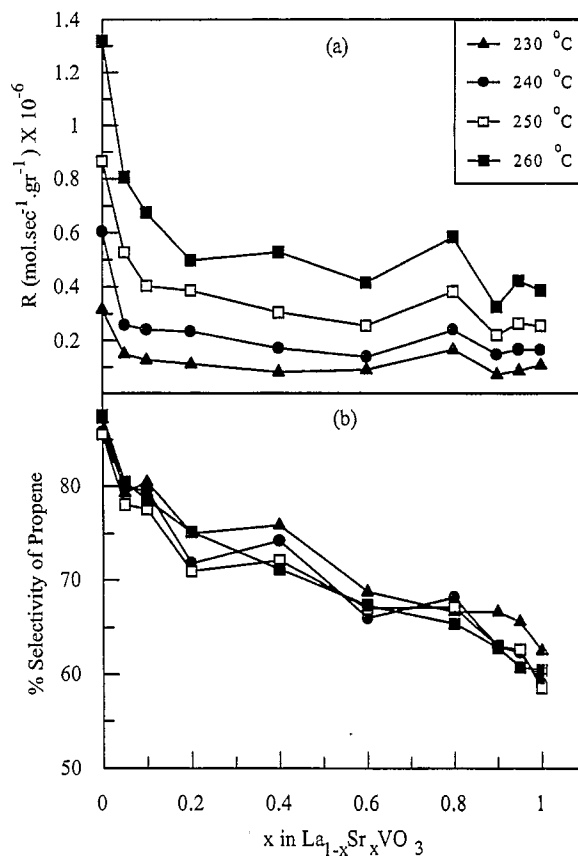


Fig. 5. (a) Reaction rate ($\text{mol s}^{-1} \text{g}^{-1}$) for the total conversion of IPA versus x in $\text{La}_{1-x}\text{Sr}_x\text{VO}_3$ solids and (b) selectivity for the production of propene versus the degree of substitution of La by Sr at the indicated temperatures.

of La by Sr. Since the propene production is related to the acid surface sites while the acetone yield is related to the basic surface sites, the picture obtained is in line with this prediction: The gradually introduction of Sr into the solid creates more basic sites and as a result increased amounts of acetone are formed.

Let us examine the situation more closely, trying to estimate in a more precise manner the acidic or basic character of perovskites $\text{La}_{1-x}\text{Sr}_x\text{VO}_3$. A quantitative parameter a characterizing the acidity or the basicity of binary oxides ABO_x was put forward by Smith [50]. According to this proposal for each reaction of the form $\text{AO}_y + \text{BO}_z \rightarrow \text{ABO}_x$ ($x = y + z$) there exists a relationship of the form $[a(\text{AO}_y)_2 - a(\text{BO}_z)_2]^2 = \Delta H_{\text{f}}^{\circ}(\text{ABO}_x)$ (kJ/mol). Furthermore, oxides with $a < -5$ are purely basic, oxides with $0 > a > -5$ are amphoteric, while for acidic oxides $a > 0$. The value of a put forward in [50] for SrO is -9.5 , while for La_2O_3 , $a = -6.1$. So the binary oxides made up of SrO should be more basic compared to those made up of La_2O_3 . Nevertheless in the later case the binary oxide LaVO_3 is also made up of V_2O_3 which must be less acidic as compared to VO_2 which participates in the formation of SrVO_3 . To estimate the a parameter for V_2O_3 and for VO_2 , whose values do not exist in [50], we made use of another relationship

proposed between a and the average electronegativity X_{eq} of an oxide, namely $a = 9.8X_{eq} - 24.5$ [51]. For VO_2 , $X_{eq} = (X_v \cdot X_o^2)^{1/3} = 2.60$ while for the V_2O_3 , $X_{eq} = (X_v^2 \cdot X_o^3)^{1/5} = 2.49$. Therefore $a_{VO_2} = 9.8(2.60) - 24.5 = 0.98$ and $a_{V_2O_3} = 9.8(2.49) - 24.5 = 0.10$. Now we can calculate the total acidic parameter for $LaVO_3$, $a(LaVO_3) = a(La_2O_3) + a(V_2O_3) = -6.10 - 0.10 = -6.2$ while for $SrVO_3$, $a(SrVO_3) = a(SrO) + a(VO_2) = -9.5 + 0.98 = -8.52$. So the more basic binary oxide $SrVO_3$ ($a = -8.52$) results in 40–45% selectivity towards acetone while the less basic material $LaVO_3$ ($a = -6.20$) provides only 10–15% acetone and 85–90% propene.

An additional point examined was the activation energies for the IPA conversion. The relevant Arrhenius plots were drawn according to relationship:

$$\ln[x - 21.94 \ln(1 - x)] = (-E_{total}/RT) + \ln(AMP_t/F) \quad (1)$$

where x is the degree of conversion, A the preexponential factor of the Arrhenius equation ($k = A_{exp}(-E_A/RT)$), M the mass of the perovskite used, P_t the total pressure in the reactor, F the feed rate (mol/s) and $E_{total} = E_A - \Delta H_{IPA}$. Eq. (1) can be easily formed as described in detail elsewhere [20,21] assuming first order kinetics for the IPA decomposition:

$$R = kP_{IPA} \quad (2)$$

as usually done for this reaction and making use of the plug-flow reactor design equation $Fdx = Rdm$ as well as the experimental conditions. Then plots of the left-hand part of equation (2) versus $1000/T$ provides excellent straight lines from which the values of E_{total} have been calculated and cited in Table 1. Plots of the log of the production rate of propene (R_{prop}) and acetone (R_{acet}) versus $1000/T$ enable us to calculate also the activation energies for these routes. There are also found in Table 1. In Fig. 6 the values of E_{total} (total conversion), E_{prop} (propene production) and E_{acet} (acetone production) have been plotted versus the degree of substitution x of La by Sr.

We observed that the activation energies for the total conversion (E_{total}) are almost identical to those calculated for the production of acetone (E_{acet}) and almost similar to those found by other researchers for the conversion of IPA on zeolites-X [48,49], with the exception of the sample $La_{0.6}Sr_{0.4}VO_3$ which shows abnormally high values of E_{acet} (163.9 kJ/mol). The values found for E_{acet} are larger as compared to E_{prop} by an almost steady amount of 10–15 kJ/mol on average, again with the exception of the $La_{0.6}Sr_{0.4}VO_3$ sample. These results are the other way around as compared to the findings by Bond and Flanzer [35] for the same reaction on V_2O_5/TiO_2 solids and by Ouqour et al. [31] on mixed cobalt and nickel molybdates. In those cases E_{acet} was found to be smaller than E_{prop} by almost 20 kJ/mol.

A common compensation effect is observed for the production of both acetone and propene as shown in Fig. 6b. According to a recent proposition put forward by Patterson and Rooney [52] such effects can be the result of the variation of the heats of adsorption ΔH_{ads} on the catalyst surface, which in effect influence the

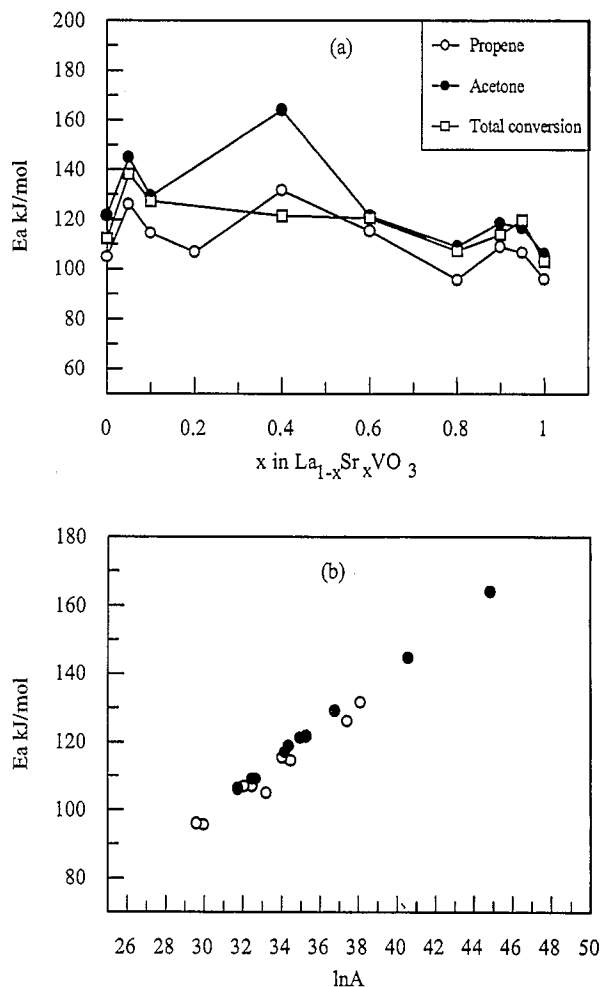


Fig. 6. (a) The calculated apparent activation energies for the total conversion of IPA (\square), the propene production (\circ) and the acetone production (\bullet) versus x . (b) Compensation effect for propene (\circ) and acetone (\bullet) production.

entropy of adsorption ΔS_{ads} . Namely an increment in ΔH_{ads} decreases ΔS_{ads} and vice versa. In our case the system is rather complicated containing five different kinds of molecules (IPA , H_2 , H_2O , acetone, propene) and it not clear which of them mainly influences the apparent activation energies via its adsorption on the surface. As a suggestion it may be the water that is more strongly adsorbed on the more basic sites that might be responsible for the production of acetone. This would have as an effect the relative increment of the apparent activation energy for the production of acetone as shown in Fig. 6. This increment is on average 10–15 kJ/mol and, according to this suggestion, is a measure of the retarding or poisoning action of water formed by the parallel reaction of the dehydration on the acetone production.

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