# Selective synthesis of vinyl ketone over SnO$_2$ nanoparticle catalysts doped with rare earths

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## Abstract

Ultrafine particles of tin oxide, doped with the rare earths Ce, Y and La respectively, were prepared using the polymeric precursor method. The novel application of nanostructured tin oxide, undoped and doped, to the C–C bond formation of an α,β-unsaturated compound (methyl vinyl ketone; MVK) is presented. The promotion of SnO$_2$ by rare earths results in a large increase in the catalytic activity and basicity (total basic sites). The catalytic behavior observed in SnO$_2$ samples suggests that the control of the catalytic activity and the selectivity of the products takes place by the segregation of a layer of a rare earth compound, with the increase of the heat-treatment temperature. The structural variations of the ultrafine particles were characterized by means of BET, XRD, CO$_2$ chemisorption and Raman.
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## 1. Introduction

The structure knowledge of metal oxide nanoparticles is a basic requirement to improve the characteristics of usual catalysts. The metal oxides, such as tin oxide-based material have been known for a long time to display good activity toward the CO/O$_2$ and CO/NO reactions [1–3]. Tin(IV) oxide exhibits redox catalytic properties by its own right, and these may be modified substantially by the incorporation of heteroelements. Such elements include Cu, Pd, Cr and Sb (for total oxidation of carbon monoxide and hydrocarbons), Sb, Bi, Mo, and V (for the partial oxidation and ammoxidation of hydrocarbons) and P and Bi (for oxidative coupling and oxidative dehydrogenation) [1–3].

Tin oxide nanoparticles, undoped and doped with rare earths (Ce, La and Y) have been investigated in our laboratory [4,5]. It was recently showed that the modification of the nanometric-scale structure and the composition of particles leads to interesting selectivity changes for the methanol

decomposition [5]. However, the influence of the nature of the active sites (the surface basicity of the oxide), on the performance of the catalysts was not investigated. The study of basicity, in more sensitive reactions, is very important as a source of information about the different kinds of active sites.

Harrison and coworkers [6,7] investigated the CO$_2$ chemisorption on tin(IV) oxide, tin(IV) oxide-palladium and tin(IV) oxide silica. These studies indicated significant differences in the behavior of the oxides, in particular the Bronsted acidity sites of the oxides. Adsorption studies employing CO$_2$ should provide further information regarding the comparative nature of the surfaces of doped tin oxide particles, especially the acid–base sites, which are also important in several catalytic processes [6].

The method reported by Ueda and coworkers [8,9] is widely applied for synthesizing vinyl ketones. It utilizes basic metal oxides (such as MgO, SrO, CaO and La$_2$O$_3$) as effective catalysts for the vinylation of ketones. This route allowed the catalytic C–C bond formation for the synthesis of α,β-unsaturated compounds, by using methanol (as a vinylating agent), accompanied by both dehydrogenation and dehydration processes. Catalytic syntheses of α,β-unsaturated compounds from olefins are economically

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attractive, due to the several applications as raw materials for many synthetic organic processes [10–12].

The aldolization reaction is promoted not only by basic sites but also by acidic sites of the transition metal supported on metal oxide catalysts. Thus, it may be suggested that the control of surfaces and modifications of the nanostructures of the tin oxide particles, undoped and doped with rare earths used as catalysts in this reaction, can be used to obtain additional information on the catalytic properties and application of these nanostructured materials.

## 2. Experimental

### 2.1. Synthesis of ultrafine tin oxide

Doped and undoped $SnO_2$ particles were synthesized by the polymeric precursor method [4,5]. This method is based on the chelation of cations (metals) by citric acid, in a water solution containing tin citrate, in the present case. Ethylene glycol is added later, in order to polymerize the organic precursor. The aqueous tin citrate solution was prepared from $SnCl_2 \cdot 2H_2O$ (Mallinckrodt Baker, USA, purity >99.9%) and citric acid (Merck, Germany, purity >99.9%) with a citric acid/metal ratio of 3:1 (in mol). For the synthesis of the rare earth-doped $SnO_2$ particles, an aqueous solution of a rare earth citrate was prepared from a rare earth nitrate (Y, La and Ce-nitrates, Alfa Aesar, USA, purity >99.9%) and citric acid with a citric acid/metal ratio of 3:1 (in mol). The aqueous rare earth citrate solution was added in the proper amount to the aqueous tin citrate solution in order to obtain a doping level of 5 mol% in all the cases. Ethylene glycol was added to the citrate solutions, at a mass ratio of 40:60 in relation to the citric acid, to promote the polymerization reaction. After several hours of polymerization at temperatures at the 90–120 °C range, the solid resin was treated at 300 °C for 6 h, in an air atmosphere.

The polymeric precursors were heat treated in two steps, initially at 300 °C for 6 h in air to promote the pre-pyrolysis, and then at several temperatures for 2 h also in air to allow the organic material to be completely oxidized and to promote the crystallization of the $SnO_2$ phase.

### 2.2. Characterization

The $N_2$ adsorption isotherms at liquid $N_2$ temperature, and $CO_2$ adsorption isotherms at 27 and 300 °C were determined in an Autosorb-1C (Quantachrome Instruments). The amount of irreversible $CO_2$ uptake was obtained from the difference between the total adsorption of $CO_2$ on the catalyst and a second adsorption series of $CO_2$ determined after evacuation of the catalyst sample for 20 min at the same temperature.

X-ray diffraction (XRD; Siemens, D5000, equipped with graphite monochromator and Cu Kα radiation) was used for the crystal phase determination. For the transmission electron microscopy (TEM), 200 kV model CM200 Philips, Holland study, a drop of the powder suspension was deposited on a carbon-covered nickel grid. Raman data were taken on a RFS/100 Bruker FT-Raman with Nd:YVO$_4$ laser providing an exciting wavelength at 1064 nm. The spectral resolution was $4\,cm^{-1}$. All the measurements were taken at room temperature.

### 2.3. Catalytic measurements

Gas phase catalytic vinylation of acetone to methyl vinyl ketone (MVK) was carried out in a fixed-bed continuous flow reactor made of stainless steel, at atmospheric pressure (300 °C) and loaded with 0.1 g of catalyst. Catalysts were first heated in a flow of helium up to 350 °C, and maintained at that temperature for 1 h. The reaction gas was composed of acetone and methanol at a 1:2 molar ratio; the total flow rate of reaction gas was $60\,cm^3/min$, with He as the carrier gas. Products were analyzed during 4 h of the continuos catalytic reaction by gas chromatography (SHIMADZU 14B GC instrument) with a flame ionization detector and a CBP1 column.

## 3. Results

The characterization of undoped and rare earth (Ce, La and Y)-doped tin oxide nanoparticles was reported earlier [4,5]. Fig. 1 illustrates the XRD patterns of the phase evolution of the $SnO_2$ particles undoped and doped with Ce, Y and La, annealed at different temperatures. Diffraction peaks related to secondary phases were observed at temperatures higher than 900 °C, suggesting the formation of a solid solution bellow that temperature, for all the different dopants. The heat treatment promotes a segregation process, resulting in a surface with a different chemical composition [5].

Fig. 2 shows low magnification bright field (BF) transmission electron microscopy images of Y-, La- and Ce-doped $SnO_2$ particles and undoped $SnO_2$ particles, annealed at 550 °C. These figures reveal that the present materials present nanometric particle sizes.

The Raman spectra of undoped and doped tin oxide samples annealed at 550 and 1100 °C for 2 h are shown inFig. 3a and 3b. The comparative analysis of the Raman bands shows the more intense bands in the samples treated at 1100 °C, what leads to the formation of nanocrystalline particles with higher crystallite size, as illustrated in Table 1. In Fig. 3a (low annealing temperature) is shown the predominance of the bands characteristic of the surface modes [13]. Fig. 3b, corresponding to $SnO_2$ samples annealed at 1100 °C shows a pronounced band at about $630\,cm^{-1}$, corresponding to the $A_{1g}$ mode, and two bands at 773 and $472\,cm^{-1}$ corresponding to $B_{2g}$ and $E_g$ modes, respectively. These results are in accordance with literature values [14]. In the Ra-
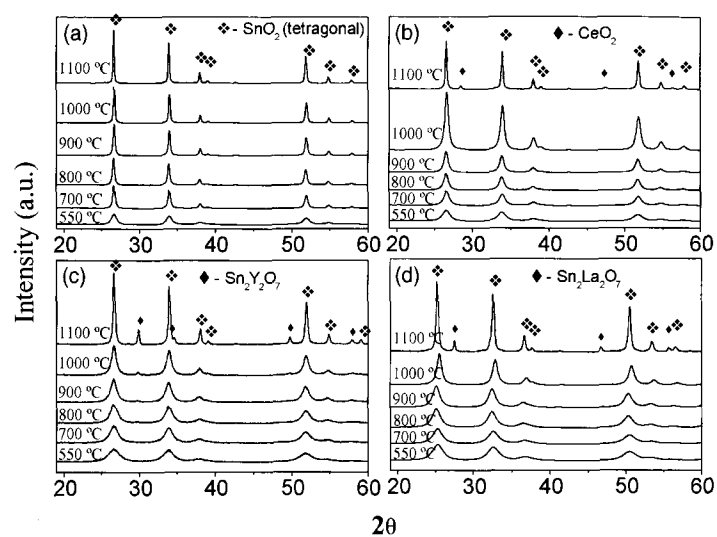
Fig. 1. Phase evolution of the undoped $SnO_2$ (a), $Ce\text{-}SnO_2$ (b), $Y\text{-}SnO_2$ (c), and $L\text{-}SnO_2$ (d) systems as a function of the heat-treatment temperature. Soaking time of 2 h.
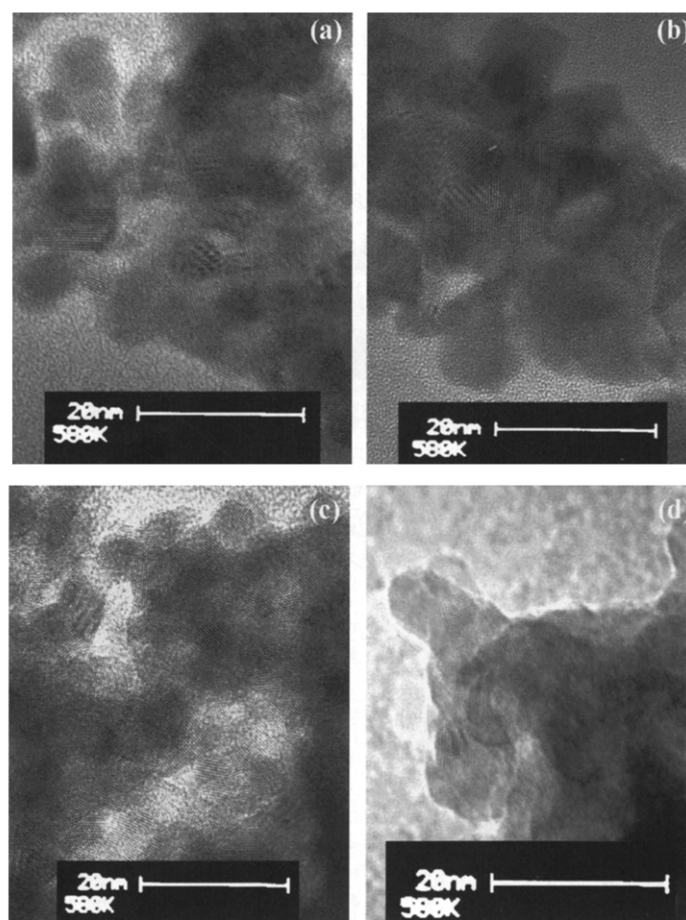


Fig. 2. TEM images of the pure (a), Ce-doped (b), La-doped (c) and Y-doped $SnO_2$ (d) powders, respectively, obtained by polymeric precursor method and heat treated at 550 °C.
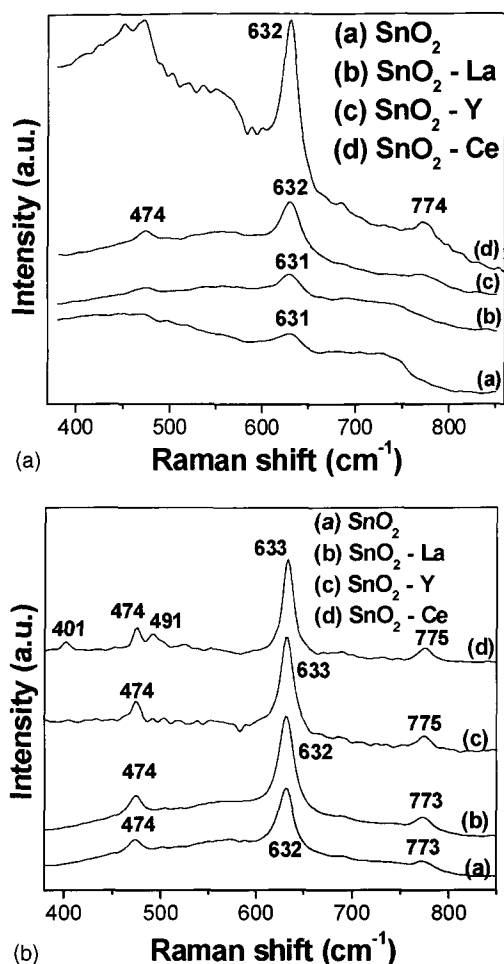
Fig. 3. Raman spectra of the undoped and doped SnO₂ samples annealing at (a) 550 °C and (b) 1100 °C.

Table 1
Crystallite sizes measured by the Rietveld refinement and BET specific surface areas as a function of the annealing temperature

| Samples | Crystallite size (Å) | | Specific surface area (m²/g) | |
|---|---|---|---|---|
| | 550[a] | 1000[a] | 550[a] | 1000[a] |
| SnO₂ | | 659.5 | 24 | 8 |
| Ce-SnO₂ | 117.2 | 194.5 | 48 | 16 |
| La-SnO₂ | 62.0 | 146.5 | 56 | 23 |
| Y-SnO₂ | 52.2 | 143.4 | 63 | 17 |

[a] Annealing temperature (°C).

Table 2
Acetone conversion (at 300 °C/during 4 h) of SnO₂ samples undoped or doped with different rare earths at different annealing temperatures

| Samples | Acetone conversion (%) ±0.2 | |
|---|---|---|
| | 550[a] | 1000[a] |
| SnO₂ | 2.5 | 0.5 |
| Ce-SnO₂ | 6.2 | 5.5 |
| La-SnO₂ | 7.3 | 4.8 |
| Y-SnO₂ | 9.9 | 4.5 |

These values were determined by means average of acetone conversions during 4 h reaction time.

[a] Annealing temperature (°C).

man spectra of Fig. 3b it was also observed that the contributions of surface modes decreased with higher annealing temperature.

The profiles of typical Raman bands of undoped and Ce-doped SnO₂ (illustrated in Fig. 3b, samples annealed at 1100 °C) are not similar. The Raman spectrum of the Ce-doped SnO₂ sample obtained by an annealing treatment of 1100 °C showed additional bands at 401 and 491 cm⁻¹. These differences are considered to be related to different electronic states promoted by the CeO₂ segregation at the higher annealing temperature. A similar perturbation of the Raman spectra was reported by Cabot et al. [13], which denotes the influence of the transition metal cations on the bulk structure of tin oxide, as a function of thermally treated materials.

3.1. Formation of methyl vinyl ketone from acetone

The rare earth doping promoted an increase in the conversion of acetone, it observed for all catalysts treated at 550 and 1000 °C (Table 2). This behavior is followed by an increase of the BET specific surface area. It is evident that the introduction of rare earths leads to a decrease in the crystallite size (Table 1) and an increase in acetone conversion. The best properties were observed with Y-doped SnO₂ treated at 550 °C. The conversion of acetone for the Y-doped SnO₂ sample is higher than for the undoped SnO₂ sample annealed in similar conditions.

Conversely, for the samples treated at 1000 °C in similar catalytic conditions, the Ce-doped SnO₂ sample showed the highest acetone conversion value.

With the increase of the annealing temperature, from 550 to 1000 °C, all the samples presented a decrease in the acetone conversion. On the other hand, if we consider the specific surface area, we can see that all rare earth-doped SnO₂ samples presented an increase in the specific activity, but the same was not observed for the undoped sample.

The aldolization reaction of acetone and methanol, promoted by SnO₂ samples leads to the C–C bond formation. In this process, occurs a subsequent reaction, which is effective to some extent for the vinylation of acetone to methyl vinyl ketone, besides forming methyl ethyl ketone (MEK) and isopropyl alcohol (IPA). However, undesirable secondary products (from the condensation and the cracking process) can be formed during the catalytic conversion of acetone [8,9]. The selectivity of this reaction can be influenced by the acidic–basic properties on the oxide surface during the cross-coupling of acetone and methanol, and by the dehydrogenation–dehydration processes preferentially on the basic surface [8]. Therefore, a basic oxide such as the La and Y oxides introduced in the SnO₂ matrix

Table 3

The total and irreversible amounts of $CO_2$ adsorption capacity, uptake at 27 and 300 °C, of undoped and doped samples of tin oxide

| Samples | Total $CO_2$ adsorption ($\mu$mol/m$^2$) | | | | Irreversible $CO_2$ adsorption ($\mu$mol/m$^2$) | | | |
|---|---|---|---|---|---|---|---|---|
| | 550[a] | | 1000[a] | | 550[a] | | 1000[a] | |
| | 27[b] | 300[b] | 27[b] | 300[b] | 27[b] | 300[b] | 27[b] | 300[b] |
| $SnO_2$ | 0.54 | 0.34 | 0.81 | 0.93 | 0.20 | – | 0.13 | 0.16 |
| Ce-$SnO_2$ | 1.66 | 0.61 | 2.05 | 1.48 | 0.76 | 0.12 | 0.45 | – |
| La-$SnO_2$ | 3.36 | 1.26 | 4.08 | 1.37 | 1.11 | – | 1.45 | – |
| Y-$SnO_2$ | 3.23 | 0.94 | 1.92 | 1.08 | 1.32 | 0.12 | 1.04 | 0.18 |

[a] Annealing temperature (°C).
[b] Isotherm temperature adsorption (°C).

will promote the basicity of the surface, besides reducing the mean crystallite size, consequently, increasing the surface area [15].

Carbon dioxide was the probe molecule used to determine the basic properties of the catalysts. The results from the isotherms of the $CO_2$ adsorption at 27 and 300 °C are illustrated in Table 3. The $CO_2$ adsorption isotherms are very sensitive to the presence of polar groups or ions on the surface of the solid [16]. It is evident that the $CO_2$ adsorption capacity of undoped $SnO_2$ samples can be significantly affected by the doping chemical species and by the annealing treatment. In the samples treated at 550 °C it was observed that the total amount of $CO_2$ adsorbed (at 27 °C) for the La- and Y-doped $SnO_2$ samples was about six times higher than that of the undoped sample.

With the increase of the heat-treatment temperature of the samples, the total $CO_2$ adsorption is favored, and thus the $CO_2$ adsorption capacities at 27 and 300 °C were changed.

It is observed that the increase of the annealing temperature leads to significant changes in the basic sites in $SnO_2$. It is important to point out the irreversible $CO_2$ adsorption uptake at 300 °C (in a similar catalytic reaction temperature) for the undoped and Y-doped $SnO_2$ samples. These results suggest that a higher annealing temperature promotes an increase of the stronger basic sites. On the other hand, for the La- and Ce-doped $SnO_2$ samples treated at 1000 °C, the isotherms taken at 300 °C did not present an irreversible $CO_2$, see Table 3. Considering these values of irreversible $CO_2$ on the $SnO_2$ samples, it was considered worthwhile to examine the selectivity of the aldolization products of the reaction of acetone with methanol.

The selectivity data for the acetone vinylation with methanol are shown in Table 4. The MVK selectivity was practically the same for the undoped and the doped $SnO_2$ samples, annealed at 550 °C. However, the selectivities for MEK, IPA and even for the cracking products of this reaction are very different. The La-doping of $SnO_2$, besides showing the highest selectivity for MVK, also decreased the formation of secondary products. With the increase of the annealing temperature of $SnO_2$ samples to 1000 and to 1100 °C, another catalytic behavior was observed, as a

Table 4

Selectivity (at 300 °C/4 h) of $SnO_2$ samples undoped or doped with different rare earths at different annealing temperatures

| Sample | AT[a](°C) | Selectivity (%) ±0.5 | | | |
|---|---|---|---|---|---|
| | | MVK | MEK | IPA | SP |
| $SnO_2$ | 550 | 62.0 | 1.0 | 11.3 | 25.6 |
| | 1000 | 56.1 | 0.0 | 18.0 | 25.8 |
| Ce-$SnO_2$ | 550 | 65.4 | 9.6 | 8.5 | 16.4 |
| | 1000 | 55.3 | 7.2 | 15.6 | 21.7 |
| | 1100 | 53.2 | 8.8 | 18.9 | 19.0 |
| La-$SnO_2$ | 550 | 66.4 | 10.8 | 9.9 | 12.8 |
| | 1000 | 64.9 | 9.8 | 13.0 | 12.2 |
| Y-$SnO_2$ | 550 | 63.2 | 12.8 | 5.0 | 18.9 |
| | 1000 | 65.1 | 5.8 | 23.1 | 5.9 |
| | 1100 | 54.1 | 5.6 | 18.3 | 22.0 |

These values were determined by means average of acetone conversion during 4 h reaction time.

[a] AT: annealing temperature; MVK: methyl vinyl ketone; MEK: methyl ethyl ketone; IPA: isopropyl alcohol; SP: secondary products.

result of the modification of the nanostructure and the basic sites of the particles. The La- and Y-doped $SnO_2$ samples annealed at 1000 °C displayed high selectivities for the MVK and also decreased the formation of cracking products. The Ce-doped (with 5.0% of acetone conversion) and Y-doped (with 4.9% of acetone conversion) $SnO_2$ samples annealed at 1100 °C presented the smallest values of MVK selectivity. This may be associated to the high amount of secondary phases ($CeO_2$ and $Sn_2Y_2O_7$, respectively) that are formed on the surface of $SnO_2$ samples, as the annealing temperature increases [4,5].

A comparative study of performed, in terms of acetone conversion including the $SnO_2$ nanoparticles prepared as previously described herein and a commercial grade $SnO_2$ from Aldrich (325 mesh, purity 99.9%). The results obtained were 2.5% for our sample and 1.5% for the commercial $SnO_2$. Poorer selectivity values were observed for the commercial $SnO_2$ sample mainly for MVK (39.2%) and MEK (0.0%), with the exception of IPA (27.0%). The values of crystallite size and BET specific surface area of the $SnO_2$ commercial sample are 113.8 nm and 7 m$^2$/g, respectively. These results indicate that the chemical and physical properties of $SnO_2$ samples depend on the surface control.

The increase of acetone conversion and the improvement of selectivity for MVK, MEK and IPA found in the doped $SnO_2$ samples can be assigned to the positive effects of rare earths (Ce, La and Y) doping. These effects include the redox properties of ceria [17], the increase of basicity on the $SnO_2$ surface promoted by the introduction of intrinsically basic sites, moreover in the cases of La [15] and Y [18]. As the annealing temperature goes up, the segregation of hetero-atoms to the surface of $SnO_2$ is enhanced, increasing the magnitude of this process. This mechanism of improvement of catalytic activity with temperature is consistent with

the observation made earlier by X-ray photoelectron spectrum (XPS) analysis [5], and also with the characterization of the catalysts performed by BET, XRD, $CO_2$ chemisorption and Raman analysis.

The surface properties, such as surface area, basicity/base strength distribution, and the catalytic activity/selectivity of rare earths promoted $SnO_2$ catalysts in the aldolization process are strongly influenced by the crystallite size, rare earth doping of $SnO_2$ and also by the annealing temperatures.

With the decrease in the acetone conversion promoted by the annealing temperature increase, one would expect a higher MVK selectivity. However, with the changes of the catalyst chemical properties, a higher MVK selectivity was observed only for the Y-doped sample. All the other catalyst samples presented a decrease of the MVK selectivity. On the other hand, the Y-doped sample annealed at 1100 °C also presented a MVK selectivity decrease.

A significant increase in the IPA selectivity was observed with the decrease in the acetone conversion. This behavior suggests that the change of the chemical properties of the catalyst surface, promoted by the annealing temperature, is unfavorable to the condensation reaction.

In the present work, it was not determined the effect of the different acetone/methanol molar ratios for all studied systems. However, this study is under way, and it will be the subject of future reports.

## 4. Conclusion

The rare earth-doped $SnO_2$ catalysts improved activity for the acetone conversion into MVK, MEK, IPA, keeping high MVK selectivity of undoped of $SnO_2$. These results were promoted by modified chemical and structural change on the surface of tin oxide nanoparticles. These modifications in the basic sites of undoped and doped tin oxide particles were revealed by $CO_2$ adsorption. These results also suggest that the modification of the $SnO_2$ catalyst by the addition of cerium, lanthanum and yttrium leads to an increase in the basicity strength of the catalysts. This strength depends of the annealing temperature of the catalysts (Scheme 1).
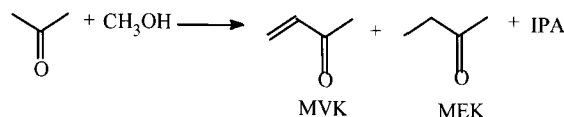


Scheme 1. Reaction of methanol and acetone, forming methyl vinyl ketone (MVK), methyl ethyl ketone (MEK) and isopropyl alcohol (IPA).

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