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Comparative Study of Catalytic Oxidation of Ethanol to Acetaldehyde Using Fe(III) Dispersed on Sb$_2$O$_5$ Grafted on SiO$_2$ and on Untreated SiO$_2$ Surfaces

Edilson V. Benvenutti *[a]*, and Yoshitaka Gushikem*[b]

aLSS, Laboratório de Superfícies Sólidas, Instituto de Química, UFRGS, C.P. 15003,

91501-970 Porto Alegre - RS, Brazil

[b]*Instituto de Química, UNICAMP, C.P. 6154, 13081-970 Campinas - SP, Brazil*

O Fe(III) foi suportado sobre o óxido de Sb(V) enxertado na superfície de sílica gel e diretamente sobre a superfície da sílica gel, respectivamente por um processo de troca iônica e de impregnação. A conversão catalítica do etanol a acetaldeído foi muito mais eficiente usando Fe/Sb/SiO$_2$ do que Fe/SiO$_2$, como catalisador. Esta maior eficiência do primeiro em relação ao segundo, leva em conta dois aspectos: a) a nova fase FeSbO$_4$ que se forma quando Fe/Sb/SiO$_2$ é submetido ao aquecimento e, b) é mais dispersa na superfície da matriz.

Fe(III) was supported on Sb(V) oxide grafted on the silica gel surface and directly on the silica gel surface using ion-exchange and impregnation processes producing Fe/Sb/SiO$_2$ and Fe/SiO$_2$, respectively. The catalytic conversion of ethanol to acetaldehyde was much more efficient using Fe/Sb/SiO$_2$ than Fe/SiO$_2$ as catalyst. This higher efficiency of the former catalyst takes into account two aspects: a) the new phase FeSbO$_4$ formed when Fe/Sb/SiO$_2$ is heat treated and, b) it is higher dispersion on the matrix.

Introduction

Studies of metallic oxides highly dispersed on the surface of inorganic supports have received special attention in recent years[1-9]. In general this kind of material presents different properties in relation to unsupported forms. In some cases, catalytic activity[5,6] and adsorption properties[7,8] improve. Another advantageous aspect is that physical properties like porosity, surface area and particle size are not substantially changed and can be monitored from the selected support.

There are several methods of synthesis to obtain dispersed metal oxides on the support surfaces: a) Impregnation[9,10] is a common process where the metal oxide is deposited over the support surface. However, this synthesis could result in a low dispersion because the metal is not bonded to the support. b) Grafting method[8,11,12] usually results in a highly dispersed form on the surface, but it can only be used when the metal (alkoxide or halide) is suffi-

ciently acidic to react with the -OH groups present on the support surface. c) Ion-Exchange method[13,14] is a very important procedure to obtain supported materials, the metal fixed on the surface by this process is always highly dispersed, because it is attracted to the surface by coulombic force at specific sites. However, it can only be used if the surface of the support shows ion-exchange properties.

In this work the iron (III) ion is fixed at the silica gel surface by two procedures: a) Impregnation and b) Ion-exchange. For the ion-exchange process, the silica gel surface was modified with antimony (V) oxide. It is known[12], that antimony (V) oxide dispersed at the silica surface presents Lewis acid sites and when hydrated, Brönsted acid sites. The Brönsted acid sites can be used to bind the iron (III) ion by ion-exchange process.

The dispersion of Fe(III) was compared for the two synthetic processes using the catalytic activity for the oxi-

dation of alcohol to acetaldehyde. The ethanol oxidation by iron (III) has already been reported[15,16].

Experimental

Antimony (V) dispersed on silica gel, Sb/SiO₂

Silica gel 60 (Merck) was activated at 150 °C under vacuum (10^{-1} Pa). The $SbCl_5$ (Carlo Erba) (6 cm³), previously distilled in a Schlenk apparatus, was dissolved in CCl_4 (Merck) (150 cm³) dried above 0.4 nm molecular sieves. The activated silica (30 g) was then added. The mixture was stirred for 20 h under dry nitrogen atmosphere at solvent-reflux temperature. The resulting modified silica was filtered in a Schlenk apparatus, washed with CCl_4 to eliminate unreacted $SbCl_5$ and trapped HCl, and finally degassed at 150 °C for 5 h. The hydrolysis of the grafted $SbCl_5$ was carried out under a flux of wet air for 48 h, then washed with bidistilled water and finally, dried for 5 h under vacuum (10^{-1} Pa) at 150 °C.

Iron(III) oxide dispersed on silica modified with antimony (V) oxide, Fe/Sb/SiO₂ (ion-exchange process)

About 30 g of Sb/SiO₂ was immersed in 100 cm³ of $FeCl_3$ 0.05 mol dm⁻³ aqueous solution (pH 1) and allowed to stand for 24 h at room temperature. The solid was filtered off, washed with bidistilled water and degassed for 5 h at 150 °C.

Iron oxide dispersed on silica gel surface, Fe/SiO₂ (impregnation process)

Silica gel 60 Merck (20 g), was immersed in an aqueous solution containing 2.8 mmol of $FeCl_3$. After drying in air at room temperature the material was degassed for 5 h at 150 °C.

Chemical analyses

The antimony and iron analyses were carried out on a Perkin Elmer 500 Atomic Absorption Spectrometer after leaching the metals from the surface with boiling concentrated hydrochloric acid. The amount of Sb and Fe, determined by atomic absorption spectrometry, were (in wt %) Fe/Sb/SiO₂: Sb = 4.5, Fe = 0.60; Fe/SiO₂: Fe = 0.72.

Specific surface area

The BET surface area of materials heated at 150 °C and 700 °C were obtained using the multipoint technique, using a Micromeritics Flowsorb 2300 instrument.

Catalytic oxidation of ethanol

The catalytic experiment was carried out under steady state. Self supporting disks of materials having an area of 5 cm² and *ca.* 50 mg were prepared. The cell was connected to a greaseless vacuum line and the system pumped for 1 h at 200 °C (10^{-2} Pa). After this treatment the catalysts were submitted to 2.7 kPa of ethanol (Merck) dried over 0.4 nm molecular sieves and 2.7 kPa of oxygen. FT-IR spectra of gas phase were obtained after heating the catalysts for 20 min. at different temperatures. The catalytic conversion was obtained from the area under the carbonyl stretching band of the acetaldehyde at *ca.* 1750 cm⁻¹. The FT-IR equipment used was a Perkin Elmer Model 1600, with 4 cm⁻¹ of resolution and a maximum of 256 scans.

Results and Discussion

The catalytic conversion was carried out in the temperature range between 200 °C and 300 °C. The spectra obtained for Fe/SiO₂ and Fe/Sb/SiO₂ are shown on Figs. 1 and 2, respectively. It can be observed in Figs. 1 and 2 that the CO stretching band increases with temperature. The main final product of catalysis was acetaldehyde, but a weak band of carbon monoxide can be observed at temperatures
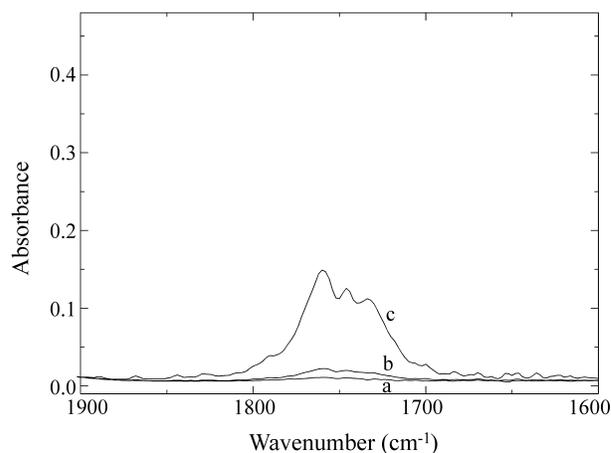

Figure 1. FT-IR gas phase spectra of the products formed in the presence of Fe/SiO₂, obtained at different temperatures: a) 200 °C; b) 250 °C; c) 300 °C.
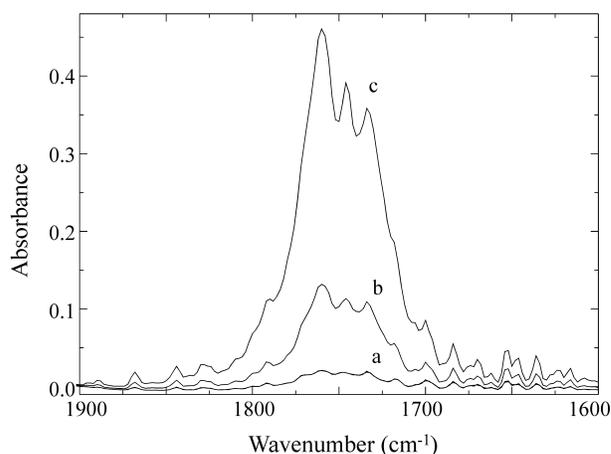

Figure 2. FT-IR gas phase spectra of the products formed in the presence of Fe/SbSiO₂, obtained at different temperatures: a) 200 °C; b) 250 °C; c) 300 °C.

more elevated than 250 °C. The pure silica gel and the Sb/SiO$_2$ (silica gel modified with antimony oxide) did not show any catalytic activity.

The catalytic activity of the materials was obtained applying the equation:

$$\mathbf{a} = \frac{\mathbf{A}\,100}{\mathbf{m}\,x} \qquad (1)$$

where $\mathbf{A}$ is the area under CO stretching band, $\mathbf{m}$ is the mass of the catalyst and x is the percent fraction of iron on the catalyst.

The catalytic activities of materials obtained from Eq. 1 at different temperatures are given on Table 1. It can be observed that Fe/Sb/SiO$_2$, obtained by ion-exchange process, converts ethanol to acetaldehyde at a temperature of 200 °C, while Fe/SiO$_2$ obtained by the impregnation method shows catalytic activity at a temperature of 250 °C. In Table 2, the ratios of catalytic activities for all temperatures is presented. It can be observed that the Fe/Sb/SiO$_2$ presents 5 times more activity than Fe/SiO$_2$.

The catalytic activity of the Fe/SiO$_2$ is lower because the iron oxide particles are agglomerated, taking into account the method of preparation and the decrease of surface area obtained before and after the thermal treatment (see Table 3). The impregnation of Fe(III) results in a decrease of the surface area even before the thermal treatment (see Table 3), and after the calcination this effect was more pronounced. It is known that the Fe(III) ions are very mobile on the silica surface[17,18] and then, the thermal treatment produces Fe$_2$O$_3$ agglomeration as larger particles, decreasing its degree of dispersion.

However, in the Fe/Sb/SiO$_2$ case, obtained by the ion-exchange process, the Fe(III) ions are fixed at specific positions of the support surface, in a highly dispersed form, since no change on the surface area was observed after the thermal treatment (see Table 3). The dispersion of the iron (III) catalyst on the silica surface considerably enhanced the catalytic activity.

The equation which describes the impregnation process is:

$$SiO_2 + mFe(OH2)_x^{3+} \rightarrow SiO_2/Fe_mO_{mx} + mxH^+ \qquad (2)$$

and the equations which describe the Fe/Sb/SiO$_2$ synthesis can be written as:

$$n{\equiv}SiOH + SbCl_5 \rightarrow ({\equiv}SiO)_nSbCl_{5-n} + nHCl \qquad (3)$$

$$({\equiv}SiO)_nSbCl_{5-n} + (5-n)H_2O \rightarrow$$
$$({\equiv}SiO)_nSb(OH)_{5-n} + (5-n)HCl \qquad (4)$$
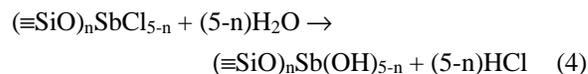
If $({\equiv}SiO)_nSb(OH)_{5-n}$ is represented by $\blacklozenge$SbOH, the reaction with the Fe(III) ion can be written as:

$$m\blacklozenge SbOH + Fe(OH_2)_n^{3+} \rightarrow$$
$$(\blacklozenge SbO)_m[Fe(OH_2)_{n-m}]^{(3-m)+} + m\,H_3O^+ \quad (5)$$

Table 2. Catalytic activity ratios.

T^a (°C)	a_2 / a_1
200	-
250	6.0
300	5.3

a = Temperature of reaction;
a_1 = Activity of Fe/SiO$_2$;
a_2 = Activity of Fe/SbSiO$_2$.

Table 3. Specific surface area.

catalysts	S_{BET} ^{a} (m^2 g^{-1})	
	(150 °C)^b	(700 °C)^b
Pure silica	395	390
Sb/SiO$_2$	372	372
Fe/Sb/SiO$_2$	380	376
Fe/SiO$_2$	366	335

a = Estimated standard deviation ± 5 m^2 g^{-1}
b = Calcinated for 5 h.

Table 1. Catalytic activity on ethanol conversion to acetaldehyde.

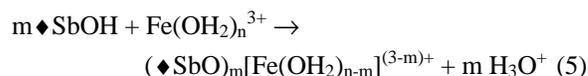| Catalyst	x^a (wt %)	m^b (mg)	T^c (°C)	A^d (abs cm^{-1})	a^e
Fe/SiO$_2$	0.72	50.1	200	-	-
			250	1.58	4.4
			300	6.24	17.3
Fe/SbSiO$_2$	0.60	46.6	200	1.22	4.4
			250	7.20	26.4
			300	25.98	92.8

a = percent fraction of iron on material;
b = mass of material;
c = temperature of reaction;
d = stretching C-O band area of acetaldehyde.

It can be observed from Eqs. 3 and 4 that Sb(V) ion is grafted on the silica surface forming a submonolayer because this ion is covalently bonded to the silica surface through the silanol group $\equiv$SiOH, forming the $\equiv$Si-O-Sb bonding. Thus, in the ion-exchange process the Fe(III) is maintained in a highly dispersed form (see Eq. 5). There is also evidence that Fe(III) in Fe/Sb/SiO$_2$ can not form Fe$_2$O$_3$ agglomerates because there is a strong interaction between iron(III) and the grafted antimony(V) on the silica surface, resulting in a new FeSbO$_4$ phase[19,20]. This last phase is presumably more effective than Fe$_2$O$_3$ in the catalytic conversion of ethanol to acetaldehyde.

Conclusions

The catalytic conversion of ethanol to acetaldehyde using Fe(III) as catalyst is more efficient when the reaction is carried out by using Fe/Sb/SiO$_2$ than Fe/SiO$_2$. This higher efficiency takes into account two aspects: a) the new phase FeSbO$_4$ formed when Fe/Sb/SiO$_2$ is heat treated and, b) The Fe(III) is better dispersed on the Fe/Sb/SiO$_2$ catalyst.

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