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Effect of tin content on silica mixed oxides: Sulfated and unsulfated catalysts

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Abstract

SnO_2–SiO_2 binary oxides were prepared by the sol–gel method, with different contents of tin oxide, and later sulfated. The resulting solids were characterized by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), surface area measurements and also titrated using Hammett indicators. To correlate the acidic properties with catalytic activity, solids were tested in the conversion of 2-propanol. Tin addition to SiO_2 produces two important effects: an increase in the surface area in most of the resulting mixed oxides and high catalytic activity for the dehydration reaction in the case of the sulfated samples.

1. Introduction

The SnO_2 has been proved to be a useful catalyst in dehydrogenation reactions providing its basic properties [1] as well as in a quite wide range of different reactions, including the oxidation of CO, saturated and unsaturated hydrocarbons and other organic compounds [2]. As expected, tin oxide is not active when used in dehydration reactions which are usually catalyzed by acid materials. The latter behavior is also found with silica gel but, however, a combination of SiO_2 with another metal oxide, for example zirconia, exhibits considerable acidity

and catalytic activity. The above is an example, among many others, where the components are inactive while their mixtures show enhanced properties if they are compared with the parent compounds. In general, according to Tanabe's hypothesis [3] generating acidity is caused by an excess of negative or positive charge in the model of a mixed oxide. Also, several authors have shown that the addition of metal oxides to silica leads to solid superacid materials with improved catalytic performance such as a high activity and resistance to deactivation [4]. Thus this work has as purpose to investigate the influence of tin oxide content in the catalytic properties of unsulfated and sulfated SnO_2–SiO_2 solid superacids using as test reaction the 2-propanol dehydration.

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2. Experimental

2.1. Catalysts

The different hydroxides used as precursors of the SnO_2–SiO_2 system were obtained, as previously reported [5], by the sol–gel procedure using tetraethylorthosilicate (Aldrich, 98%), $SnCl_2$ (J.T. Baker, 98.9%) and ethyl alcohol (Merck, 99.8%) as solvent. The dried samples with different tin oxide contents at various SnO_2–SiO_2 ratios were sulfated by impregnation with 4 ml/(g cat) of 1 N H_2SO_4 aqueous solution. The final catalysts were obtained by drying the above sulfated samples at 383 K for 24 h followed by calcination at 773 K.

2.2. Characterization

Surface area and pore size distribution were measured by the nitrogen adsorption method on a Micromeritics ASAP-2000 system. FT-IR was performed on a Nicolet 170-SX spectrometer. The sample was pressed into a thin self-supported wafer and placed in the IR cell. After evacuation at 773 K in vacuum for 2 h, the cell was cooled down to room temperature and pyridine was adsorbed using nitrogen as carrier gas, which was evacuated again to eliminate excess of pyridine and, finally, the IR spectra were registered at 323 K. The acid strength of the materials was measured by titration using Hammett indicators, dissolved in benzene, by assuming that formation of conjugate acid comes from the interaction between the acidic site in the mixed oxide, independently of its Lewis or Brønsted nature, and the basic indicator. The corresponding X-ray diffractograms of the samples were recorded with a D-500 Siemens goniometer coupled to a copper anticathode tube in order to have Cu Kα radiation provided by a diffracted beam monochromator.

2.3. Catalytic evaluation

The catalytic activity of the solids in the 2-propanol conversion at 423 K was carried out in a conventional fixed-bed continuous flow microreactor system using 0.1 g of sample (mesh 80–120) with 60 ml/min He flow as carrier gas (molar ratio of He/2-propanol is 5). Before catalytic evaluation, the samples were pretreated in situ by heating under He gas at a flux rate of 40 ml/min during 1 h at 423 K. The reaction products were analyzed on line by means of a Varian 3700 gas chromatograph equipped with a FID and using a 30 m GSQ Megabore column at 413 K.

3. Results and discussion

In the search of functional groups, the different sulfated samples calcinated at 773 K were diluted in KBr. They showed the infrared absorption spectra, at room temperature, displayed in Fig. 1. In all cases a wide band appears at 3450 cm^{-1} corresponding to the OH vibration which is ascribed to the physisorbed water in the catalyst. The flexion vibration band of the H_2O molecule occurs at 1632 cm^{-1}. Related with the SiO_2, there are four bands at 470, 800, 960 and 1097 cm^{-1}; the last one is assigned to the asymmetric stretching of the Si–O group,

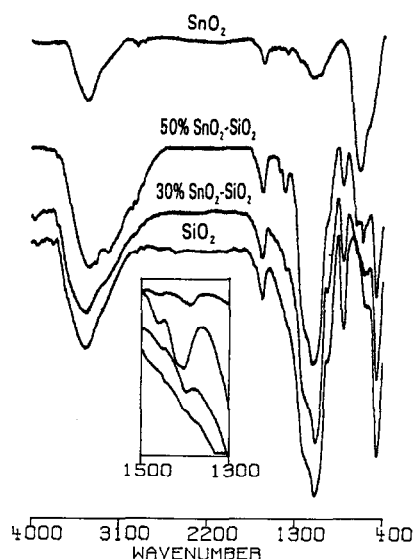Fig. 1. Infrared spectra of SO_4^{2-} /(SnO_2–SiO_2) as a function of SnO_2 content.

the band at 470 cm^{-1} is associated with the flexion vibration band of the O–Si–O group with a small signal at 960 cm^{-1} attributed to the Si–OH vibration. In the analysis of the bands referring to the sulfate ion, whose Lewis and Brønsted nature was already reported [5], it should be pointed out that the spectra corresponding to SnO$_2$ 50 wt% clearly show two different signals that can be impute to SO$_4^{2-}$. The first one occurs at 1400 cm^{-1} and belongs to the sulfate-ion bidentate coordinate with Si in good agreement with Yamaguchi et al [6]. The second one is a more intense band at 1375 cm^{-1}, which can be associated to the sulfate-ion bidentate but coordinated now to Sn. In fact, when the infrared spectra of SO$_4^{2-}$–SnO$_2$ is analyzed, the above band still appears but the one at 1400 cm^{-1} disappears because of the absence of SiO$_2$ in the sample. This result is correct under the condition that we have mixed oxides, segregated, instead of solid solutions as verified by the X-ray diffractograms shown next. However, before that, it is also necessary to mention that vibration bands of Sn–OH, around 3400 cm^{-1}, are less important when compared with the Si–OH vibration, which means a minor ability of the SnO$_2$ to hydratation. Besides, the band located at 625 cm^{-1} increases with the content of SnO$_2$ for which it is associated also to Sn.

Concerning the aforementioned segregation of phases, Fig. 2 presents the X-ray diffractograms recorded for different samples. Clearly, the SnO$_2$ cassiterite spectrum (JCPDS 21-1250 file) appears above a content of 12% SnO$_2$ in the mixed oxide and the intensity of the spectrum increases with the augmentation of the SnO$_2$ concentration. In the same way it is observed that the FWHM of the peaks decreases as the SnO$_2$ increases, which means that the crystal size increases. Additionally, the broad halo characteristic of SiO$_2$ decreases as its concentration diminishes. In other words, at low contents of tin oxide it appears clearly an amorphous zone ascribed to silica, the rutile SnO$_2$ structure which dominates when SiO$_2 \to 0$, and
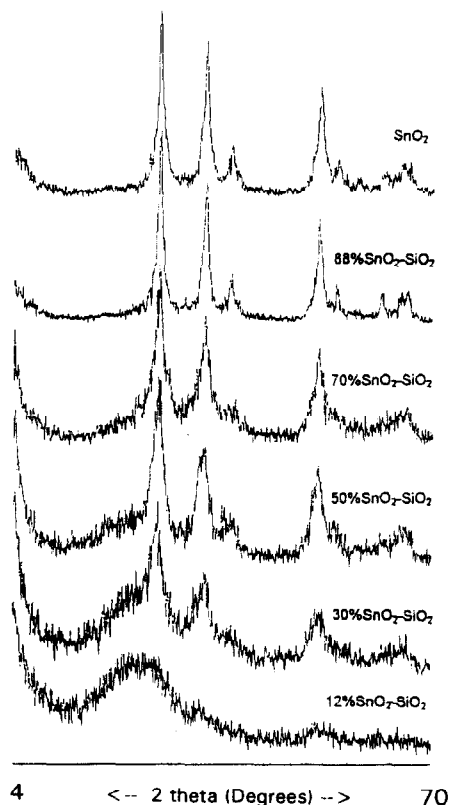

Fig. 2. X-Ray diffraction patterns of SnO$_2$–SiO$_2$ mixed oxides at different rates of single oxides.

at intermediate silica/tin oxide ratios the diffractograms are those of the mixed oxides with a contribution depending on the choice of the SiO$_2$ and SnO$_2$ content. That is, the oxides are segregated in good agreement with the fact that there are no solid solutions as precursors of tin silicate SnSiO$_3$.

In respect to the acid strength of materials, there are two particular cases to be considered: unsulfated and sulfated. In both cases, the titration results of Table 1 clearly show a remarkable increase in acidity when sulfate ion is incorporated into the samples. For unsulfated oxides, although the single component SiO$_2$ showed little acidity, mixing silica with tin oxide resulted in an enhancement in acidity, reaching a maximum at stoichiometric values around 50 wt% of each component. However, this maximum corresponds to a pK value that is lower

Table 1
Titration measurements of solid acid strength

Catalysts (wt%)	Hammett indicator					
	sulfated			unsulfated		
	2,4,6-trinitroaniline	p-nitrochlorobenzene	2,4-dinitrotoluene	2,4-dinitroaniline	benzalacetophenone	anthraquinone
SiO_2	+	−	−	+	-	−
12% SnO_2–SiO_2	+	+	+	+	+	−
30% SnO_2–SiO_2	+	+	+	+	+	−
50% SnO_2–SiO_2	+	+	+	+	+	−
70% SnO_2–SiO_2	+	+	+	+	+	−
88% SnO_2–SiO_2	+	+	+	+	−	−
SnO_2	+	+	−	+	−	−
pK_a value	− 10.1	− 12.7	− 13.7	− 4.4	− 5.6	− 8.2

+: change in color; −: no change in color.

than the one needed to consider those compounds as solid superacids. Otherwise, when the above materials are sulfated, their acidity supersedes the minimum H_O estimation for which the new solids are considered to be superacids. That is, although indicators were used up to $H_O = -13.75$, the maximum acidity of superacid materials is also in the range of stoichiometry between 50 and 70 wt% of tin oxide.

With regard to the surface area of materials, the results of sulfated and unsulfated samples are given in Fig. 3 as function of the SnO_2 content. Independent from the catalyst being sulfated or not, its surface area enlarges considerably according to the increase of tin oxide in the mixture SnO^{2-}–SiO_2. Concerning the influ-

Fig. 3. Influence of the SnO_2 content in mixed oxides with respect to the surface area in sulfated and unsulfated samples.

ence of the sulfate ion on the samples, an opposite behavior is observed for the single oxides separately: on one hand, sulfated silica strongly decreases its area while on the other hand sulfated tin oxide slightly enlarges its area. That is, sulfated mixed oxides decrease their areas when compared with the corresponding unsulfated ones. However, this fact is less important than the increasing surface area obtained when tin oxide is mixed with silica: around 200% increase in area when using 50 wt% SnO_2 and SiO_2 with respect to the samples of SiO_2 alone in the case of sulfated samples. In general, it is interesting to notice that the decrease of surface in sulfated materials has the same curved shape of the area behavior of unsulfated samples as the function of the SnO_2 content. This is due to the fact that SO_4^{2-} ions occupy sites in such a way that these serve as bridges between particles in order to increase the sintering process with the concomitant decrease of surface area.

Finally, the results of catalytic activity for the above samples, tested in the 2-propanol dehydration reaction, are given in Table 2 for sulfated and unsulfated prototypes with different tin content; selectivity towards propene is around 100% for all samples, except the unsulfated tin oxide sample, which showed also acetone in good agreement with its basic nature. According to the data, it becomes clear that an important
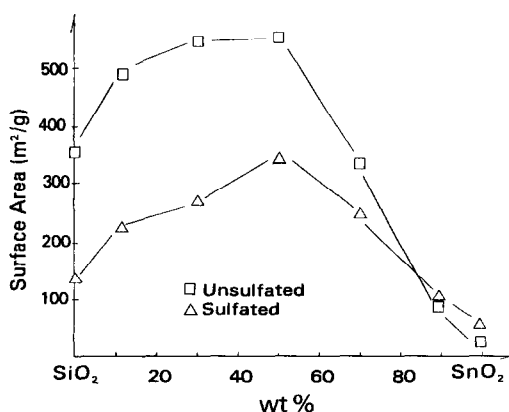
Table 2
Catalytic activity of the sulfated and unsulfated SnO_2–SiO_2 system in the 2-propanol reaction

Catalysts (wt%)	Conversion (mol%)					
	sulfated			unsulfated		
SiO_2	13.3	2.8	1.6	0.1	0.1	0.1
12% SnO_2–SiO_2	60.6	57.3	53.6	3.1	2.1	1.2
30% SnO_2–SiO_2	66.3	67.8	62.1	3.1	2.5	1.4
50% SnO_2–SiO_2	63.5	60.2	54.8	2.6	1.3	0.7
70% SnO_2–SiO_2	67.9	60.6	61.4	2.1	1.1	0.5
88% SnO_2–SiO_2	18.5	13.4	8.9	0.3	0.3	0.3
SnO_2	16.0	9.6	6.2	0.4	0.4	0.3
Reaction time (min)	15	60	180	15	60	180

Reaction Temperature: 423 K, catalyst wt.: 0.1 g, He flow: 60 cm^3/min. molar ratio He/2-propanol: 5.

increase of catalytic activity occurs when using sulfated catalysts: from 3% 2-propanol conversion for unsulfated samples to 67% for sulfated mixed oxides. This improvement in the catalytic performance of the sulfated samples is kept more or less constant in the range from 12 wt% to 70 wt% tin oxide content. Also, as can be appreciated from Fig. 3, this range of stoichiometry corresponds to the one where there is more than 100% increase in surface area of the sulfated samples when compared to the single sulfated silica. These two facts are clearly related as we will see next, but first we consider other results such the major stability of the solids. In fact, from the data in Table 2 for samples sulfated, a minor deactivation of the catalysts containing tin oxide when compared with the activity of silica is found; that is, tin

oxide helps to stabilize the catalyst. Also, due to the different surface area in silica and tin oxide, in order to compare the above conversion data, in Table 3 we consider the specific rate values which take into account the surface area that corresponds to each prototype in the mixtures. Thus, according with these results when tin oxide is added to silica, an increase of the specific activity appears as a consequence of the active sites belonging to the SnO_2 incorporated into the silica. However, when the content of tin oxide becomes large in the mixed oxide, the surface area decreases abruptly, showing that active sites function at the formation of large crystals of SnO_2 as a second surface. Finally, the SnO_2 alone gives rise to a major specific activity because the site density is higher but the site total number is the lowest, which suggests that is the tin oxide which is responsible of the catalysis.

In short, we learn from the above results that getting a mixed oxide, tin oxide–silica, by itself is not a sufficient condition to have a solid with improved strong acidic features. That is, in addition it is necessary to sulfate the above mixed oxide to obtain catalysts with improved strong acid properties. On the other hand, while unsulfated mixed oxides enlarge considerably the surface area when compared with the surface area of its single components, by itself this parameter does not constitute a sufficient condition to have a material with improved catalytic properties. As a consequence, this two single

Table 3
Activity per unit surface area of the sulfated and unsulfated SnO_2–SiO_2 system in the 2-propanol reaction

Catalysts (wt%)	Specific reaction rate (mol m^{-2} s^{-1})					
	sulfated			unsulfated		
SiO_2	5.45E − 08	1.15E − 08	6.35E − 09	2.50E − 10	2.26E − 10	2.26E − 10
12% SnO_2–SiO_2	1.51E − 07	1.42E − 07	1.33E − 07	2.68E − 09	2.42E − 09	1.36E − 09
30% SnO_2–SiO_2	1.56E − 07	1.59E − 07	1.46E − 07	3.67E − 09	2.91E − 09	1.69E − 09
50% SnO_2–SiO_2	1.19E − 07	1.13E − 07	1.03E − 07	3.08E − 09	1.51E − 09	8.56E − 09
70% SnO_2–SiO_2	1.64E − 07	1.47E − 07	1.48E − 07	4.39E − 09	2.15E − 09	1.00E − 09
88% SnO_2–SiO_2	9.40E − 08	6.80E − 08	4.60E − 08	2.63E − 09	2.38E − 09	2.21E − 09
SnO_2	2.78E − 07	1.67E − 07	1.08E − 07	7.56E − 09	6.46E − 09	5.54E − 09
Reaction time (min)	15	60	180	15	60	180

Reaction temperature: 423 K. catalyst wt.: 0.1 g. He flow: 60 cm^3/min, molar ratio He/2-propanol: 5.

features, area and acidity, have to be put together; a better catalyst will result on the condition that a higher surface area and higher acidity properties concur in the same material.

4. Concluding remarks

The purpose of this work has been twofold. On the one hand we have studied the influence of the content of SnO_2 in silica with respect to the catalytic properties of the resulting material when used as catalyst. On the other hand, the samples were also studied sulfated and unsulfated in order to compare some of their particular characteristics, due to the fact that many features of materials are closely related with the sulfation solids. According to our results, several of these features are equal, regardless of the nature of the samples. However, we found that there are others that are not necessarily the same for all compounds. For example, our results in the case of separate tin oxide and silica alone show a remarkable increase of acidity in both materials, when sulfated, but a dissimilar behavior concerning surface area; that is, while tin oxide increases its area slightly, silica decreases

it considerably. However, the greatest area of SiO_2, when compared with the one of SnO_2, makes a desirable combination of both oxides to give rise to compounds that are more active and consequently still by far more efficient when used as sulfated catalysts. In other words, in order to improve the features of a solid to be useful as catalyst both conditions are necessary to have a sulfated mixed oxide. In our case, although silica reduces its area when sulfated, it helps to improve the tin oxide area, increasing with sulfate ion the acidity of the resulting solid.

References

[1] H. Matsuhashi, M. Hino, K. Arata, Appl. Catal. 59 (1990) 205.
[2] P.G. Harrison., Chemistry of Tin, Blackie, Glasgow, London, 1989.
[3] K. Tanabe, Solid Acids and Bases; their Catalytic Properties, Academic Press, New York, 1987.
[4] K. Arata, Adv. Catal. 37 (1990) 165.
[5] P. Salas, J.G. Hernández, E. López-Salinas, I. Schifter, M.E. Llanos, J. Navarrete, J. Morales, J. Porous Mater. 3 (1996) 241.
[6] T. Yamaguchi, T. Jin, K. Tanabe, J. Phys. Chem. 90 (1986) 3148.