

CALORIMETRIC STUDY OF THE ACIDITY AND INTERFACE EFFECTS OF TIN DIOXIDE LAYERS DEPOSITED ON ANOTHER METAL OXIDE

D. Sprinceana^{1,2}, *M. Caldararu*², *N. I. Ionescu*² and *A. Auroux*^{1*}

¹Institut de Recherches sur la Catalyse, CNRS, 2 avenue Einstein, 69626 Villeurbanne Cedex, France

²Institute of Physical Chemistry, Spl. Independentei 202, 77208 Bucharest, Romania

Abstract

Samples with various amounts of tin oxide were prepared by impregnating γ -Al₂O₃, TiO₂(anatase), SiO₂, ZrO₂ and MgO with tin tetrachloride or tributyltin acetate solutions. After drying and calcination, the samples were characterized by chemical analysis, XRD and BET measurements. Ammonia adsorption microcalorimetry was used in order to determine the number, strength and strength distribution of surface acid sites. The influence of the adsorption temperature, evacuation temperature, amount of SnO₂ deposited and of the nature of the support on the adsorption properties were studied.

Keywords: acid sites, calorimetry, surface, tin dioxide

Introduction

The systems obtained by depositing SnO₂ on various supports present a great practical interest because of their widespread use for conductive coatings, gas sensors, solar cells, electronic devices and as catalysts [1-3].

Despite the obvious interest for the use of a higher surface area SnO₂ (usually obtained by supporting it) there are very few systematic studies on the influence of the loading and of the nature of support on the adsorption properties of the resulting materials [1, 4-7]. In the present paper, we have investigated the acid properties of materials obtained by deposition of different amounts of tin dioxide on several metal oxide supports. This study will help in understanding the effect of the acid-base nature of supports on the performance of supported SnO₂ catalysts, as the selection of the support is an important step in the design of industrial catalysts. Beside the microcalorimetric measurements of the heat of ammonia adsorption, the samples were characterized by chemical analysis, XRD and BET measurements.

Experimental

We have used five supports having different acid/base characteristics with a surface area around 100 m² g⁻¹ as follows: γ -Al₂O₃, TiO₂ (anatase), SiO₂, ZrO₂ and

* Author to whom all correspondence should be addressed.

MgO. One of our aims was to obtain a highly dispersed deposit of SnO₂ with a minimum decrease of the surface area of the resulting material with respect to the support. The impregnation was made using solutions of tin tetrachloride pentahydrate (TCP) (Aldrich) in distilled water [8, 9]. After drying, the samples were heated in oxygen flow for 6 h at 423 K and for 8 h at 773 K. The amounts of tin deposited were determined by chemical analysis and presented as mass percent of Sn. Two parallel series of samples were prepared: one with a low content of SnO₂ (~3 wt% Sn) and the other one with a higher loading (~20 wt% Sn) where SnO₂ may possibly form a continuous layer on the substrate. The samples used in our experiments together with the BET surface area (measured by nitrogen adsorption) and the Sn content are presented in Table 1.

Table 1 Supports and supported SnO₂ materials used in microcalorimetric measurements

Origin/Precursor	Material	Amount Sn/wt%	S _{BET} m ² g ⁻¹
BDH	SnO ₂	99.9	9.0
Oxid C (γ), Degussa	Support A (γ-Al ₂ O ₃)	0	130
DT 51, Rhone Poulenc	Support B (TiO ₂)	0	103
Aerosil 130, Degussa	Support C (SiO ₂)	0	130
ZrO ₂ 137, Degussa	Support D (ZrO ₂)	0	90
Carlo Erba	Support E (MgO)	0	120
TCP	A1-SnAl (SnO ₂ /Al ₂ O ₃)	3.1	108
TCP	A3-SnAl (SnO ₂ /Al ₂ O ₃)	19.2	89
TCP	B1-SnTi (SnO ₂ /TiO ₂)	3.4	90
TCP	B3-SnTi (SnO ₂ /TiO ₂)	25.4	59
TCP	C1-SnSi (SnO ₂ /SiO ₂)	3.2	112
TCP	C3-SnSi (SnO ₂ /SiO ₂)	21.7	96
TCP	D1-SnZr (SnO ₂ /ZrO ₂)	3.4	78
TCP	D3-SnZr (SnO ₂ /ZrO ₂)	18.6	63
TCP	E1-SnMg (SnO ₂ /MgO)	3.7	54
TCP	E3-SnMg (SnO ₂ /MgO)	23.5	25

The acidity of the samples was tested by using NH₃ as probe molecule for adsorption. Adsorption measurements were performed in a heat flow microcalorimeter of the Tian Calvet type (model C80 from Setaram) linked to a conventional volumetric apparatus, as described in detail elsewhere [10].

By measuring amounts adsorbed at increasing pressures and the heat evolved in the adsorption of each one of the subsequent doses of adsorbate, the volumetric isotherm and differential heats of adsorption vs. adsorbed amount were simultaneously obtained.

Before each experiment the samples were outgassed overnight at 673 K in a vacuum better than 1 mPa. Experiments were carried out at 423 K unless otherwise stated. Adsorption was extended up to an equilibrium pressure of about 130 Pa. After the adsorption was completed, pumping at the temperature of the experiment and consecutive readsorption of ammonia at the same temperature were performed in order to determine the chemisorbed amount. Amounts adsorbed are expressed as micromoles of molecules per gram of sample.

Results and discussion

The commercially available BDH bulk SnO_2 that we have preliminary tested has a very low surface area ($9 \text{ m}^2 \text{ g}^{-1}$). The differential heat, Q_{diff} , at the beginning of ammonia adsorption being 230 kJ mol^{-1} proves the presence of the most acid sites among our samples (Fig. 1). However a partial reduction of the tin oxide surface by ammonia itself (or during the pretreatment) may also have occurred contributing to a modification of the surface and such high heats. The heats remain relatively constant, above 200 kJ mol^{-1} , up to a coverage of $1.5 \mu\text{mol m}^{-2}$ and then decrease abruptly to reach the physisorption domain.

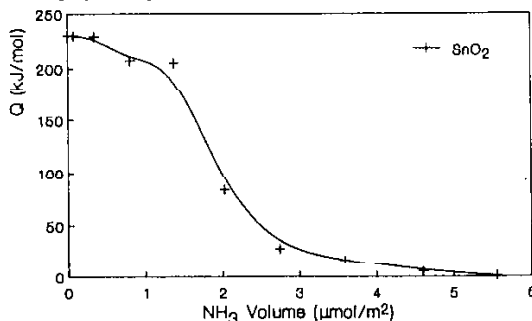


Fig. 1 Differential heats of NH_3 adsorption at 423 K vs. the adsorbed volume on SnO_2 pretreated at 673 K

Prior to any impregnation, the acidity of the supports was investigated also by NH_3 adsorption (Figs 2 and 3). As expected MgO (known as a basic support) and SiO_2 (almost inert) showed the lowest acid properties as evaluated by strength and number of sites (Fig. 2). The most acidic samples, zirconia and anatase, behaved rather similarly with respect to ammonia adsorption showing a plateau of differential heat around $130\text{--}150 \text{ kJ mol}^{-1}$. Alumina, a typically amphoteric solid characterized by the presence of both acid and basic sites [11] displays a differential heat curve with high initial heats followed by a continuous decrease with coverage.

Figure 3 represents the corresponding volumetric adsorption isotherms. As can be seen SiO_2 and MgO present nearly no vertical section in which the uptake increases at negligible equilibrium pressures. On the contrary, the ZrO_2 and TiO_2 samples present a large vertical section characteristic of strong chemisorption. The alumina curve is located between these two sets of curves.

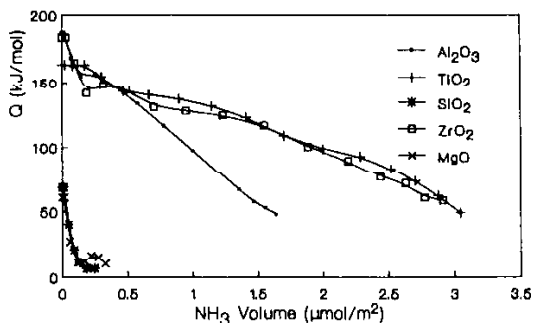


Fig. 2 Differential heats of NH_3 adsorption at 423 K vs. the adsorbed volume on the supports pretreated at 673 K

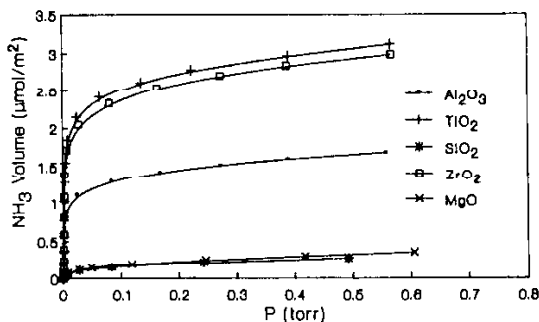


Fig. 3 Isotherms of NH_3 adsorption at 423 K on the supports pretreated at 673 K

We have investigated the differences between samples obtained by impregnation of the various supports with aqueous solutions containing various amounts of TCP. From the point of view of surface area there are no significant differences between the samples when the loading is increased from 3 to 20 Sn wt% except with TiO_2 and particularly with MgO (Table 1). On low loaded samples we could not find the characteristic XRD lines for SnO_2 which suggests an acceptable dispersion on the support, but the XRD diffraction pattern are different for the high SnO_2 loading, probably because of a poor dispersion of SnO_2 and the presence of crystallites. However, no any evidence for the presence of SnO or metallic Sn was shown by XRD analysis for the fresh samples. We have also characterized our samples by solid state NMR spectroscopy and we did not found any signal specific of the presence of SnO even after carrying catalytic tests for depollution with the samples.

In Figs 4 and 5 are represented the heats of NH_3 adsorption on samples with low (~ 3 wt% Sn) and high (~ 20 wt% Sn) SnO_2 loadings respectively on the various supports. On the SiO_2 support the addition of SnO_2 enhances the heat evolved at the beginning of adsorption and new acid sites are formed in the whole range of differen-

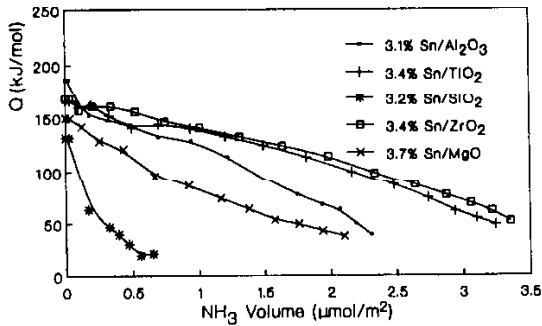


Fig. 4 Differential heats of NH_3 adsorption at 423 K vs. the adsorbed volume on the low SnO_2 loaded samples pretreated at 673 K

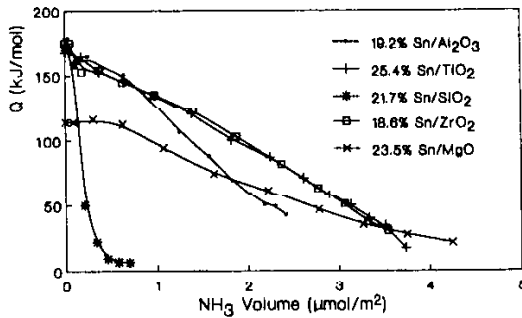


Fig. 5 Differential heats of NH_3 adsorption at 423 K vs. the adsorbed volume on the high SnO_2 loaded samples pretreated at 673 K

tial heat between 20 and 170 kJ mol^{-1} . A small amount of tin oxide enhances considerably the acidity but the increase of the loading from 3 to 20 wt% Sn has less influence. However the adsorbed ammonia volume remains the lowest of the series of samples.

The most dramatic change of the overall acidity by increasing the amount of deposited Sn was observed for the MgO based samples in spite of the important reduction of the surface area. For E3-SnMg one obtains the most important adsorbed ammonia uptake at high coverage in the series of our samples. A small amount of tin oxide creates strong acid sites with heats above 150 kJ mol^{-1} while a high loading increases drastically the number of medium and weak acid sites but decreased the strength and number of strong acid sites. This can be explained by a poor dispersion of SnO_2 at the surface of the high loaded sample giving rise to an average heat at the beginning of the adsorption.

The series of materials using titania and zirconia as supports are similar in their behavior. The presence of SnO_2 on these supports produces only very small increases of the acidity, more visible at low loading than at high loading.

Since SnO_2 is widely used for resistive gas sensors a higher attention was paid to γ -alumina supported samples.

The acidity characterization has proved that the deposition of SnO_2 on Al_2O_3 increases the number of acid sites on the support in the 50–130 kJ mol^{-1} domain of differential heats (Q_{diff}) but did not affect the heats of adsorption at low coverage. Moreover the increase of Sn loading from 3% to 20% did not change significantly the acidity. In any case, the differential heats were much lower than for the SnO_2 bulk oxide.

We have also investigated by microcalorimetry the influence of the pretreatment temperature on the surface acidity of γ - Al_2O_3 and A3-SnAl samples. The increase of the temperature of evacuation from 473 to 573 and finally to 673 K has increased the amount of adsorbed ammonia by increasing the number of strong acid sites available for adsorption (Fig. 6). In fact, the number of sites giving rise to an evolved heat higher than 140 kJ mol^{-1} is varying from 0.05 to 0.3 and then 0.8 $\mu\text{mol m}^{-2}$ with increasing temperature. The dependence of the adsorption isotherm on the evacuation temperature is mainly determined by the modification of the support during the outgassing. The guest oxide has less influence. However at the same outgassing temperature, covering alumina with tin dioxide creates a parallel shift of the isotherm to higher adsorbed ammonia uptakes

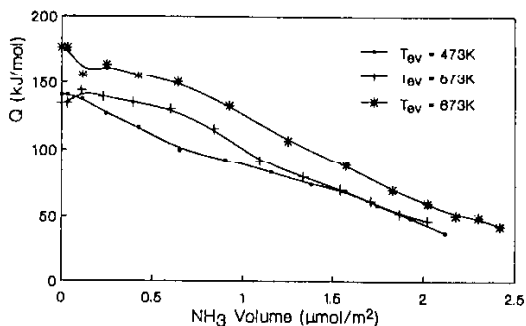


Fig. 6 Differential heats of NH_3 adsorption at 423 K vs. the adsorbed volume on A3-SnAl samples pretreated at 473, 573 and 673 K

For the A3-SnAl sample we have performed the calorimetric measurements at four different temperatures (Fig. 7). By increasing the adsorption temperature the volume of adsorbed ammonia decreases because the adsorption can take place only on sites with higher strength. It is a way to determine the strongest acid sites of the studied sample. The common aspect of the differential heat curves for all cases can be outlined. At low adsorbed amounts a decrease of the adsorption heat takes place in a short uptake range. After the initial decrease of the heat of adsorption a plateau is observed and its importance and extension vary, being important at 323 K. It becomes insignificant at 563 K demonstrating the heterogeneity of the sample surface and supporting the assumption that the interaction of the probe molecule with surface Lewis acid sites is the main contribution to the adsorption heat at this tempera-

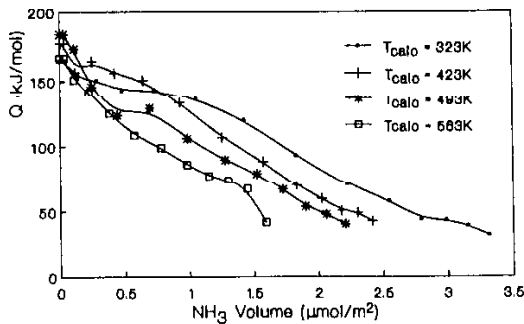


Fig. 7 Differential heats of NH_3 adsorption at 353, 423, 493 and 563 K vs. the adsorbed volume on A3-SnAl samples pretreated at 673 K

ture. The relative position of the differential heat curves follows the order one may expect as a function of the temperature.

Conclusions

By supporting tin dioxide on various supports it was possible to obtain high surface area SnO_2 containing materials. The properties of resulting samples are strongly determined by the support. Supporting SnO_2 on TiO_2 and ZrO_2 did not result in an appreciable change in the acidity. A remarkable increase was obtained for SiO_2 and MgO . Alumina was mainly modified in the medium acid strength domain. The amount of deposited tin dioxide has less influence; an increase from 3 to 20 wt% Sn does not reinforce significantly the acidity, but for the magnesia samples.

* * *

The authors are thankful to Dr. B. Bonnetot (Laboratoire de Physico-Chimie Minérale, Univ. Claude-Bernard, Lyon I, France) for his invaluable advice and help in the samples preparation.

References

- 1 T. Tagawa, S. Kataoka, T. Hattori and Y. Murakami, *Appl. Catal.*, 4 (1982) 1.
- 2 D. F. Cox, T. B. Fryberger and S. Semancik, *Phys. Rev. B*, 38 (1988) 2072.
- 3 D. W. Niles, D. Rioux and H. Höchst, *J. Appl. Phys.*, 73 (1993) 4586.
- 4 T.-C. Sheng, P. Kirszensztejn, T. N. Bell and I. D. Gay, *Catal. Letters*, 23 (1994) 119.
- 5 P. Kirszensztejn, W. Przystajko and T. N. Bell, *Catal. Letters*, 18 (1993) 391.
- 6 V. M. Jiménez, J. A. Mejias, J. P. Espinós and A. R. González-Elipe, *Surface Science*, 366 (1996) 545.
- 7 J. Shen, R. D. Cortright, Y. Chen and J. A. Dumesic, *Catal. Letters*, 26 (1994) 247.
- 8 Nouveau traité de chimie minérale, P. Pascal (Ed.), Vol. VIII, Masson et C^{ie}, Paris 1963, p. 300.
- 9 B. Gergely and A. Auroux, *Res. Chem. Intermed.*, 25 (1999) 13.
- 10 A. Auroux, *Topics in Catalysis*, 4 (1997) 71.