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MICROCALORIMETRIC STUDIES OF THE SURFACE REACTIVITY OF POLLUTANT GAS ATMOSPHERES ON SUPPORTED SnO_2 AND Ga_2O_3 CATALYSTS

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Abstract

The surface properties of gallium oxide and tin dioxide supported on alumina or titania have been studied by adsorption microcalorimetry. The differential heats of adsorption of various pollutant adsorbates such as sulfur dioxide, nitrogen monoxide, nitrogen dioxide and also ammonia were measured on these catalytic surfaces. NH_3, SO_2, NO_2 are strongly adsorbed while NO is only physisorbed. The supported Ga_2O_3 samples show a slight decrease in acidity as probed by ammonia adsorption, compared to alumina or titania. The addition of SnO_2 decreases the number of strong acid sites but creates a few weak and medium strength acid sites on alumina and does not modify the acidity of titania. In all cases, the basicity, probed by SO_2 adsorption, is very strongly affected by the deposition of Ga_2O_3 or SnO_2. The differential heats of NO_2 adsorption remain nearly constant on all samples. The heats of adsorption are discussed as a function of the coverage and of the amount of guest oxide.

Keywords: adsorption microcalorimetry, Ga_2O_3, NH_3, NO_2, SnO_2, SO_2

Introduction

The NO decomposition over Cu/ZSM-5 and noble metal catalysts has been investigated in various studies [1], but the metal exchanged zeolites are not highly stable. Moreover the reaction inhibition and catalyst deactivation in the presence of oxygen and water have not been solved out. Finally, the selective catalytic reduction (SCR) of NO_x using ammonia is not practical and safe.

The need to reach the future stricter emission standards prompted us to search for catalysts able to provide an alternative to metal exchanged zeolites or noble metal catalysts, able to reach a low temperature reduction (below 400°C) and able to avoid the N_2O formation which is an undesirable side reaction (particularly for platinum catalysts).

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It is known that the addition of active metal on alumina enhances the lower temperature performance for NO reduction by hydrocarbons or NO decomposition [2]. In another work we have demonstrated [3] that Ga and Sn are active for nitrogen oxides reduction with hydrocarbons on various non-zeolite supports such as alumina and titania. It has also been shown that the activity of oxide based catalysts can be attributed to their acidity. The type of surface precursor complex formed during the reaction depends on the type and strength of the acidity available on the surface of the catalyst. In this regard the cooperation between alumina and the active metal center has to be investigated too.

Tin oxide surfaces have been extensively studied by Harrison [4], McAleer [5] and Chiorino [6]. Physicochemical properties of gallium oxide have been reported in many studies [7] and gallium supported alumina catalysts have been recently studied for NO reduction by hydrocarbons [2, 8]. Catalysts consisting of bulk tin oxide and alumina modified by tin ions have been studied by various techniques such as MAS NMR [9], pyridine infrared spectroscopy [10], XPS and FTIR study of SO_2 adsorption [11], calorimetry [12, 13] and catalysis [14, 15].

The various gases known to be involved in depollution reactions are NO, NO_2, SO_2, NH_3, H_2O, O_2 and hydrocarbons. These gases are not invariably chemisorbed, and the interaction with the surface can be a weak or strong form of chemisorption. In this work, the adsorption properties of alumina and titania based gallium and tin catalysts have been investigated using mainly adsorption microcalorimetry.

Experimental

Commercial γ-alumina (oxid C from Degussa) and titania (DT 51 from Rhône-Poulenc anatase) were used as host oxides. The supported oxides were prepared by impregnation using $Ga(NO_3)_3{\cdot}9H_2O$ and $SnCl_4{\cdot}5H_2O$ (Aldrich) as precursor salts in aqueous solution. After impregnation the catalysts were dried at 120°C overnight and calcinated at 500°C for 5 h under dioxygen flow.

The composition and the physical properties of the catalysts are summarized in Table 1. The surface area (BET) was determined by the standard nitrogen adsorption at –196°C. The chemical composition was measured by plasma emission spectroscopy. Mössbauer spectroscopy was used to control the valence states of tin in the SnO_2/Al_2O_3 samples.

The microcalorimetric studies were performed in a heat flow calorimeter (C80 from Setaram) at 353 K for NH_3 and SO_2 adsorptions and at 298 K for NO_2 and NO adsorptions. A detailed description of the technique has been reported elsewhere [16]. The microcalorimeter is linked to a volumetric adsorption line, equipped with a Barocel capacitance manometer for pressure measurements. The samples were outgassed at 673 K for 3 h prior to microcalorimetric measurements. The differential heats of adsorption were measured as a function of coverage by sending repeated doses of gas onto the samples until an equilibrium pressure of about 66 Pa was reached. Then the sample was evacuated for 1 h at the same temperature and a second adsorption was performed in order to allow the determination of chemisorption uptakes. Ammonia was purified by successive freeze-thaw pumping cycles. Sulfur dioxide, nitrogen dioxide and monoxide (Air Liquide, purity of 99.9%) were used without further purification.

Results and discussion

A summary of the compositions and surface areas of the samples is presented in Table 1. Addition of tin or gallium oxide on alumina did not significantly affect the surface areas of the support. The titania based catalysts are more affected, mainly at high loading.

Table 1 Chemical composition and surface properties of the different samples

Samples	Ga^{3+} or Sn^{4+}/ wt%	Surface area/ $m^2 g^{-1}$	Coverage/ μmol ion m^{-2}
γ-Al_2O_3		112	
GaAl 0.2	0.24	126	0.3
GaAl 2	2.1	112	2.7
GaAl 9	8.6	109	11.3
GaAl 18	18.3	108	24.3
GaAl 34	33.9	108	45.0
Ga_2O_3	74.4	81	
SnAl 0.2	0.24	118	0.2
SnAl 2	2.1	113	1.6
SnAl 8	8.3	115	6.0
SnAl 12	11.5	102	9.5
SnAl 24	23.7	94	21.2
SnO_2	78.8	58	
TiO_2		108	
GaTi 5	5.3	89	8.5
GaTi 14	14.0	78	25.7
GaTi 22	22.6	67	48.4
SnTi 5	5.0	91	4.6
SnTi 12	12.3	83	12.5
SnTi 21	21.3	71	25.3

Deposition of a second oxide on the carrier leads to the transformation of its structure, which then involves changes in the quantity and strength of interaction between the carrier and the guest oxide deposited on its surface. As a result of these changes, the physicochemical character of the carrier can also change (acid-base properties, adsorption properties, ...), thus affecting the catalytic process. Since the activity of a catalyst is proportional to its effective surface area exposed to reactants, all the adsorption data are reported in μmol of adsorbed gas per m^2 of catalyst surface.

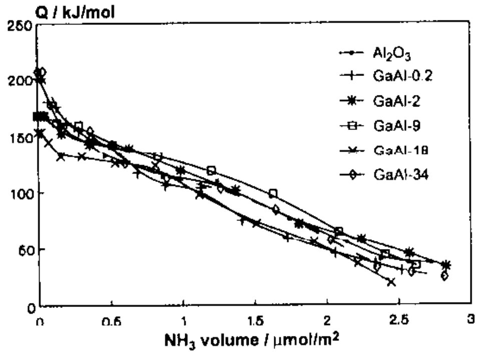

Fig. 1 Differential heats of ammonia adsorption *vs.* coverage for Ga_2O_3/Al_2O_3 samples

Figure 1 represents the differential heats of adsorption as a function of the ammonia uptake for the various samples of gallium oxide deposited on alumina. The acidity of bare alumina is not much affected by the addition of gallium oxide. The heats of adsorption at low coverage or at high coverage show a tendency to decrease with the loading, except for the most loaded sample (GaAl-34), which as seen by XRD is not well dispersed. However, in the domain of middle acid strength (around 120 kJ mol^{-1}) the heats of adsorption and the number of acid sites increase slightly with the loading, reaching a maximum around 9 wt% of Ga. Because the experiments were performed at a slightly lower temperature than for usual acidic materials (353 K instead of 423 K usually), the ability of ammonia to interact with weak sites as well as with strong sites may be responsible for the observation of a continuous decrease of the differential heats as a function of coverage and the absence of a well-defined plateau.

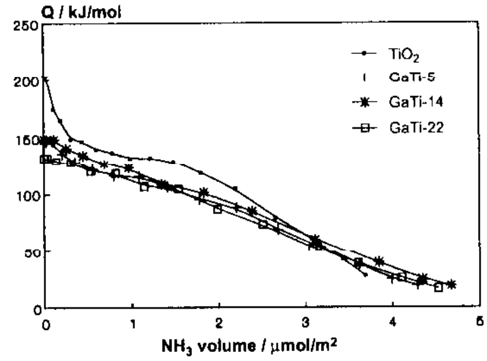

Fig. 2 Differential heats of ammonia adsorption *vs.* coverage for Ga_2O_3/TiO_2 samples

Figure 2 represents the heats of adsorption of ammonia on the gallium oxide samples deposited on titania. Compared to bare titanium oxide, it can be seen that both the heats and the number of sites are decreased when gallium oxide is added, mainly in the domain of strong sites (above 100 kJ mol^{-1}). However the loading amount does not seem to play a determinant role as the three curves are nearly identical.

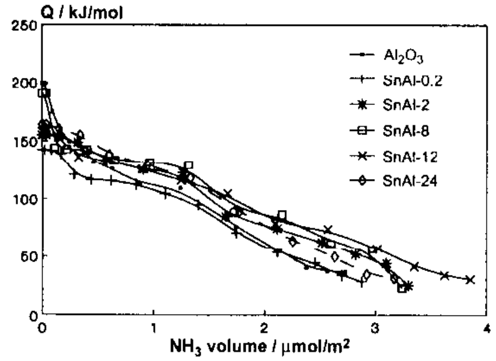

Fig. 3 Differential heats of ammonia adsorption *vs.* coverage for SnO_2/Al_2O_3 samples

When tin oxide is added to alumina (Fig. 3), the heats of adsorption and number of acid sites increase slightly in the domain of intermediate strength and weak acidity (below 130 kJ mol^{-1}), except for sample SnAl-0.2 which displays lower heats of adsorption in the whole range of coverage. However, at very low coverage, the addition of SnO_2 to γ-Al_2O_3 decreases the number of strong acid sites (heats of ammonia adsorption higher than 140 kJ mol^{-1}). These results are in agreement with a similar study from Shen *et al.* [13].

Except for the initial heats of adsorption which are decreased, the addition of tin oxide on titanium oxide does not create any modification in the number and strength of acid sites as can be seen in Fig. 4.

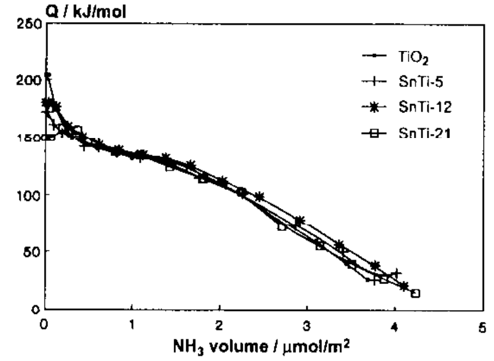

Fig. 4 Differential heats of ammonia adsorption *vs.* coverage for SnO_2/TiO_2 samples

The calorimetry data concerning the adsorption of sulfur dioxide on gallium oxide samples on alumina are shown in Fig. 5. The differential heats are relatively con-

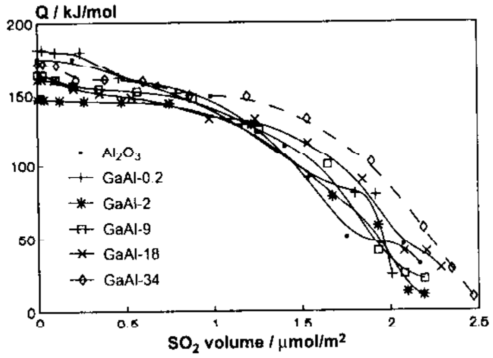

Fig. 5 Differential heats of sulfur dioxide adsorption *vs.* coverage for Ga_2O_3/Al_2O_3 samples

stant, showing a plateau in the 150–170 kJ mol^{-1} domain. The initial heats are smaller than on bare alumina except for sample GaAl-0.2. For this sample, the slightly higher heats found at low coverage may result from defects in the oxide structure and the occurrence of a doping effect. At high coverage, it can be seen that the total amount adsorbed increases with the amount of gallium oxide. If sulfur dioxide can be regarded as an acidic probe, it means that the addition of gallium oxide either creates new basic sites or that gallium oxide is more bonded to the acid sites than to the basic sites of alumina, creating a loss of acid sites in alumina [17].

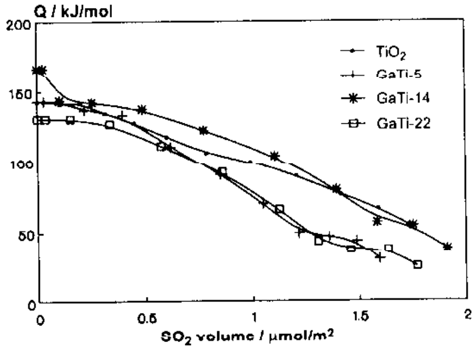

Fig. 6 Differential heats of sulfur dioxide adsorption *vs.* coverage for Ga_2O_3/TiO_2 samples

Figure 6 represents the differential heats of adsorption *vs.* SO_2 uptake on the titania supported gallium oxides. The samples GaTi-5 and GaTi-22 display very similar curves in the whole range of coverage, with a total number of basic sites lower than on bare titania.

The calorimetry data for the adsorption of SO_2 on alumina supported tin oxides are given in Fig. 7. On all samples, the differential heats are significantly smaller

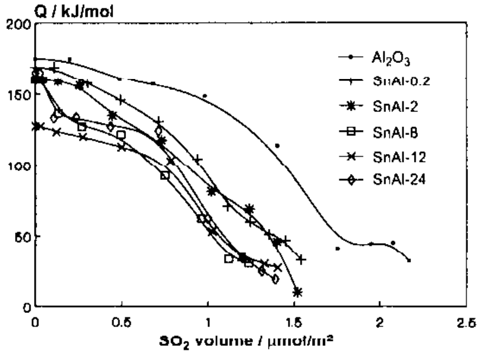

Fig. 7 Differential heats of sulfur dioxide adsorption *vs.* coverage for SnO_2/Al_2O_3 samples

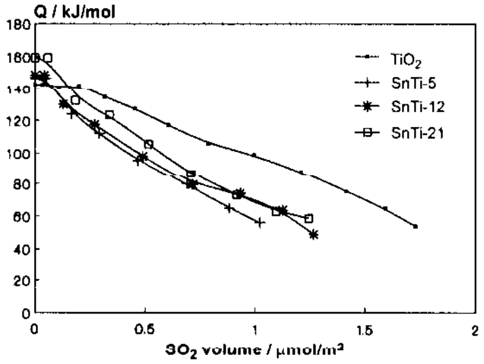

Fig. 8 Differential heats of sulfur dioxide adsorption *vs.* coverage for SnO_2/TiO_2 samples

than on alumina at any coverage. Both the strength and the number of basic sites are decreased with increasing amount of tin oxide.

Tin oxide supported on titanium oxide also creates a decrease in the number of basic sites as can be seen in Fig. 8 which represents the differential heats of SO_2 adsorption *vs.* coverage. Tin oxide seems to create more heterogeneity in the site strength distribution. The slightly higher heats found at low coverage may indicate that tin oxide is mainly anchored on the basic sites of the amphoteric titania, as the acidity is not affected by the addition of tin oxide (Fig. 4). So the loading decreases the number of the basic sites and not their strength. A bad dispersion of tin oxide at the surface of titania may explain the similarity of the curves of the three supported oxides.

Figure 9 represents the differential heats of adsorption of nitrogen dioxide *vs.* coverage for the GaAl series. Because of the high reactivity of NO_2, the experiments were performed at 298 K only. Even at this low temperature, a reaction began to occur at high coverage, perhaps between the adsorbed molecules, creating a bell shaped curve. This high reactivity occurred mainly on bare alumina and to less extent on the

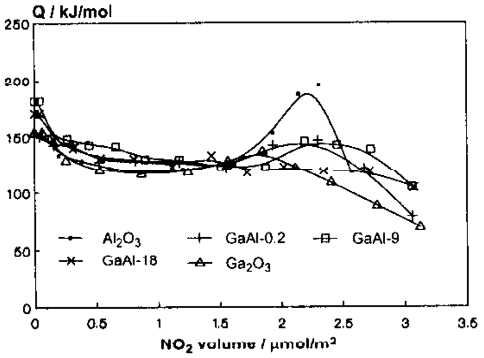

Fig. 9 Differential heats of nitrogen dioxide adsorption *vs.* coverage for Ga_2O_3/Al_2O_3 samples

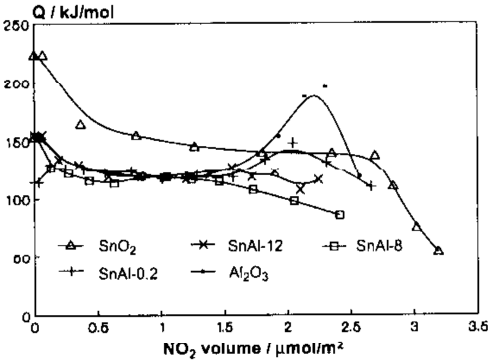

Fig. 10 Differential heats of nitrogen dioxide adsorption *vs.* coverage for SnO_2/Al_2O_3 samples

supported oxides and on pure gallium oxide. In the domain of low coverage the heats are relatively constant, around 140 kJ mol^{-1}, and similar for all gallium loadings.

The differential heats of NO_2 adsorption *vs.* coverage are represented in Fig. 10 for alumina supported tin oxides. The heats are all close to 130 kJ mol^{-1} at low coverage. At high coverage the bell shape is evidenced only for the least loaded sample (SnAl-0.2) while it does not occur on the more loaded samples (SnAl-8 and SnAl-12) and on pure tin dioxide.

The differential heats of NO adsorption on all samples belong to the physisorption domain. All the adsorbed NO amount can be easily removed by pumping and the heats remain in the range of 40–15 kJ mol^{-1}.

Conclusions

It has been demonstrated that ammonia, sulfur dioxide and nitrogen dioxide are strongly adsorbed by all the samples while NO is only physisorbed. When gallium oxide is supported on alumina, the number of acid sites decreases slightly, while the number of basic sites increases but not their strength. On the contrary, when supported on titania, gallium oxide causes a decrease in the number of basic sites, and does not affect the amount of acid sites but only their strength. Alumina supported tin oxides show a decrease of basicity both in number and strength and a slight increase of the number of weak and medium strength acid sites. Tin dioxide supported on titania creates a decrease in the number of basic sites but does not affect the strength nor the acidity. In all cases the basicity is more disturbed than the acidity. The effects of increased loading amounts are more marked on alumina than on titania.

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