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Microcalorimetric and infrared spectroscopic studies of γ-Al_2O_3 modified by tin oxides

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Microcalorimetric and infrared spectroscopic studies of ammonia and carbon dioxide adsorption have been used to study the effects on the acid/base properties of adding tin oxide to γ-Al_2O_3. 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), increases the number of weaker acid sites (heats from 110 to 130 kJ/mol), and decreases slightly the number of basic sites (heats of carbon dioxide adsorption from 70 to 150 kJ/mol). In contrast, the presence of SnO on γ-Al_2O_3 decreases the total number of acid sites (heats of ammonia adsorption higher than 70 kJ/mol) and eliminates most of the basic sites. Infrared spectroscopy of adsorbed ammonia reveals interactions between aluminum cations and stannous ions, leading to a decrease in the strength of the Lewis acid sites associated with aluminum cations.

Keywords: acidity; basicity; microcalorimetry; ammonia; carbon dioxide; γ-Al_2O_3; SnO; SnO_2

1. Introduction

Catalysts consisting of Pt and Sn supported on γ-Al_2O_3 have been widely studied for reforming and dehydrogenation reactions [1–5]. For example, the addition of tin to platinum catalysts enhances the selectivity for the aromatization reactions and increases catalyst stability. Much work has been conducted regarding the chemical state and the role of tin in $PtSn/Al_2O_3$ catalysts [6–12]. For example, it has been established that tin can be stabilized as Sn(II) in alumina [3,6–9], and it has been suggested that tin modifies the acidity of the alumina support [6,12].

In this present study, we have investigated the effect of tin on the acid/base property of γ-Al_2O_3. In particular, we have employed microcalorimetric measurements of the heats of ammonia and carbon dioxide adsorption to measure the number and strength of acid and base sites, respectively. In addition, we have used infrared

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spectroscopy to study the chemical states of these adsorbed molecules to determine the nature of the acid and base sites. In a previous work, we studied the acid/base properties of γ-Al_2O_3 modified by K_2O, MgO and La_2O_3 [13].

2. Experimental

The surface area of the γ-Al_2O_3 (Davison) studied was 200 m^2/g. A sample containing about 1000 μmol Sn per gram of γ-Al_2O_3 was prepared by impregnating γ-Al_2O_3 with a methanol solution of tributyltin acetate (Aldrich), followed by drying at 393 K overnight and calcining at 573 K for 2 h and 723 K for 6 h. The Sn/Al_2O_3 sample exhibited the X-ray diffraction pattern of the initial γ-Al_2O_3, indicating that tin oxide was highly dispersed.

Mössbauer spectroscopy was used to monitor the valent states of tin following various treatment conditions. The Mössbauer spectra were collected at room temperature using an Austin Science Associates model S-600 Mössbauer spectrometer. The spectrometer was operated in constant acceleration mode with a 10 mCi single line γ-ray source of $Ca^{119m}SnO_3$ (Amarsham). Detection of the γ-rays was achieved with a Xe–CO_2 proportional counter. A palladium filter was placed in the radiation beam to absorb X-rays from the source. The spectrometer was calibrated with $BaSnO_3$ and β-Sn standard absorbers. Isomer shifts are reported relative to $BaSnO_3$.

Microcalorimetric studies of the adsorption of NH_3 and CO_2 at 423 K were carried out using a Tian-Calvet heat-flux apparatus, which has been described elsewhere [14]. The microcalorimeter was connected to a gas-handling and volumetric adsorption system, equipped with a Baratron capacitance manometer for precision pressure measurements. The differential heat of adsorption versus adsorbate coverage was obtained by measuring the heats evolved when doses of gas (2–5 μmol) were admitted sequentially onto the catalyst until the surface was saturated by adsorbed species.

Ammonia was purified by successive freeze/pump/thaw cycles. Carbon dioxide with a purity of 99.99% (Anaerobe, AGA Specialty Gases & Equipment) was used without further purification. Before microcalorimetric measurements, the samples were typically dried under vacuum at 573 K for 1 h, calcined in 500 Torr O_2 at 723 K for 6 h and evacuated at 723 K for 1–2 h. The γ-Al_2O_3 treated in this way was designated as $Al_2O_3(O)$. The SnO/Al_2O_3 sample was obtained by reducing the sample in H_2 at 753 K. For comparison, the γ-Al_2O_3 was also treated in H_2 at 753 K and was designated as $Al_2O_3(R)$.

Infrared spectra were collected with a Nicolet FX 7000 FTIR system equipped with a liquid-nitrogen cooled MCT detector. Each spectrum was recorded at 2 cm^{-1} resolution with 32 co-added scans. Sample pellets were formed with a thickness of 20–30 mg/cm^2. The samples were loaded into a quartz cell equipped with CaF_2 windows, followed by the same sample treatments used for microcalorimetric

adsorption studies. Ammonia and carbon dioxide were then dosed onto the sample at 423 K for 0.5 h. The cell was then isolated, cooled to room temperature and evacuated sequentially at 298, 373 and 473 K. Infrared spectra were collected after each evacuation.

3. Results and discussion

Mössbauer spectra of the Sn/Al_2O_3 sample as-prepared and reduced in H_2 at different temperatures are shown in fig. 1. The corresponding Mössbauer parameters are given in table 1. After calcination at 723 K for 6 h, the sample exhibited a doublet with an isomer shift of 0.06 mm/s and a quadrupole splitting of 0.91 mm/s, which can be assigned to SnO_2. Reduction of this sample in H_2 at 723 K reduced 82% of the SnO_2 to SnO as determined by the change of intensity of the SnO_2 peak.

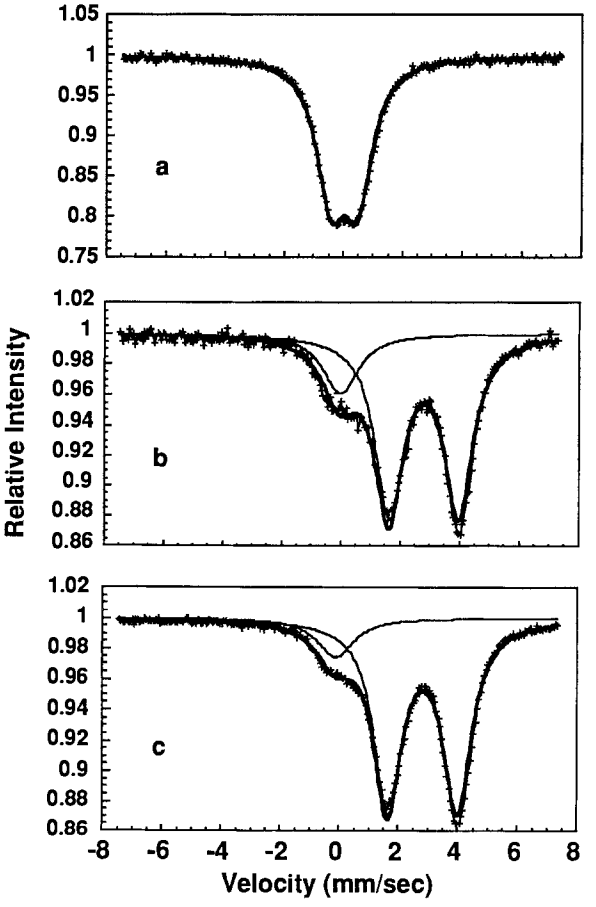

Fig. 1. Mössbauer spectra of Sn/Al_2O_3 after: (a) calcination in O_2 at 723 K for 6 h, (b) reduction in H_2 at 723 K for 4 h, and (c) reduction in H_2 at 753 K for 4 h.

Table 1
Mössbauer spectroscopy parameters of SnO_2/Al_2O_3 and SnO/Al_2O_3 samples

Treatment	Mössbauer parameters				Assignment
	δ[a] (mm/s)	Δ[b] (mm/s)	width (mm/s)	area (%)	
723 K, O_2, 6 h	0.06	0.91	1.18	100	SnO_2
723 K, H_2, 4 h	0	–	1.46	18	SnO_2
	2.83	2.35	1.15	82	SnO
753 K, H_2, 4 h	−0.13	–	1.49	12	SnO_2
	2.83	2.35	1.15	88	SnO

[a] δ = isomer shift.
[b] Δ = quadrupole splitting.

The peaks associated with SnO have an isomer shift of 2.83 mm/s and a quadrupole splitting of 2.35 mm/s. Bacaud et al. [6] observed similar Mössbauer parameters for SnO_2 and SnO on alumina. Further reduction in H_2 at 753 K increased the content of SnO to 88%. These Mössbauer experiments showed no indication of Sn metal (isomer shift of 2.55 mm/s) after reduction at either 723 or 753 K. Based on these Mössbauer spectroscopy results, calcination at 723 K in O_2 and reduction at 753 K in H_2 were employed to obtain samples for microcalorimetric measurements that consisted primarily of SnO_2 and SnO, respectively on γ-Al_2O_3.

Fig. 2 shows the differential heats of adsorption versus coverage of ammonia on γ-Al_2O_3, SnO_2/Al_2O_3, and SnO/Al_2O_3. The initial heat of ammonia adsorption on γ-Al_2O_3(O) was approximately 155 kJ/mol. The addition of SnO_2 decreased the initial heat of ammonia adsorption to 145 kJ/mol. Moreover, SnO_2 decreased the strength of stronger acid sites and increased the strength of intermediate and

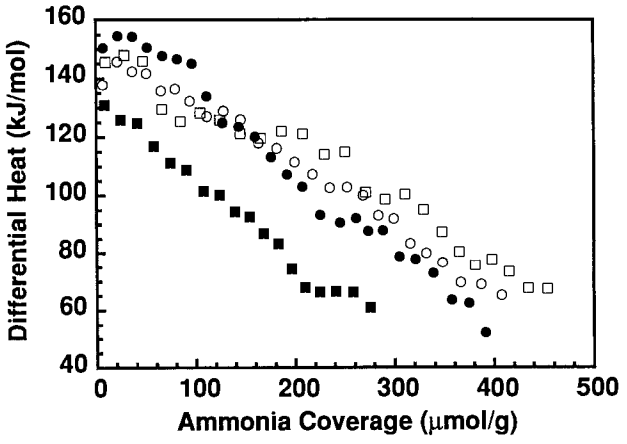

Fig. 2. Differential heat versus adsorbate coverage for adsorption of NH_3 at 423 K on γ-Al_2O_3 calcined at 723 K (●), γ-Al_2O_3 treated in H_2 at 753 K (○), SnO_2/γ-Al_2O_3 (□), and SnO/γ-Al_2O_3 (■).

weak acid sites. Treatment of γ-Al_2O_3 in H_2 at 753 K also decreased the initial heat of ammonia adsorption to about 145 kJ/mol, but the treatment did not affect sites of intermediate strength and weak acid sites on γ-Al_2O_3. The different behavior of the γ-Al_2O_3(O) and γ-Al_2O_3(R) samples is probably caused by the different temperatures employed in these treatments, i.e., 723 and 753 K, respectively. In contrast to the SnO_2/Al_2O_3 sample, the SnO/Al_2O_3 sample showed a decrease in the total number of acid sites on γ-Al_2O_3. The initial heat of ammonia adsorption decreased from 155 to 130 kJ/mol and the total coverage of ammonia decreased from about 400 μmol/g to less than 280 μmol/g upon the reduction to SnO.

The microcalorimetric results of carbon dioxide adsorption on γ-Al_2O_3, SnO_2/Al_2O_3, and SnO/Al_2O_3 are shown in fig. 3. The initial heat of CO_2 adsorption on γ-Al_2O_3 was about 145 kJ/mol. The addition of SnO_2 decreased the heat of CO_2 adsorption on essentially all base sites and decreased the saturation CO_2 coverage from 80 to 55 μmol/g. Treatment of γ-Al_2O_3 in H_2 at 753 K did not influence the subsequent adsorption of CO_2. However, the presence of SnO significantly decreased the basicity of γ-Al_2O_3. The initial heat of CO_2 adsorption decreased from 145 to 110 kJ/mol, and the saturation CO_2 coverage decreased from 80 to 25 μmol/g.

Fig. 4 shows histograms of the apparent distribution of site strengths for ammonia and carbon dioxide adsorption on γ-Al_2O_3, SnO_2/Al_2O_3, and SnO/Al_2O_3. The histograms were obtained by first fitting the data of differential heat versus coverage by a polynomial and then using the fitted polynomial to determine the amount of adsorbates adsorbed within a given range of differential heats. The histograms for ammonia adsorption show that γ-Al_2O_3 exhibits a wide range of heats of adsorption. The addition of SnO_2 decreases the number of sites with differential heat near 150 kJ/mol and increases the number of sites with differential heat near

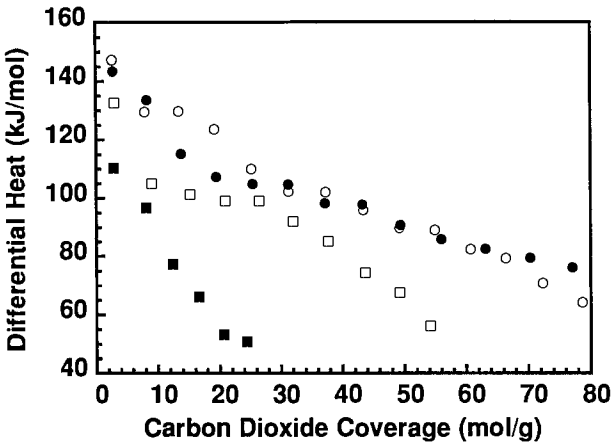

Fig. 3. Differential heat versus adsorbate coverage for adsorption of CO_2 at 423 K on γ-Al_2O_3 calcined at 723 K (●), γ-Al_2O_3 treated in H_2 at 753 K (○), SnO_2/γ-Al_2O_3 (□), and SnO/γ-Al_2O_3 (■).

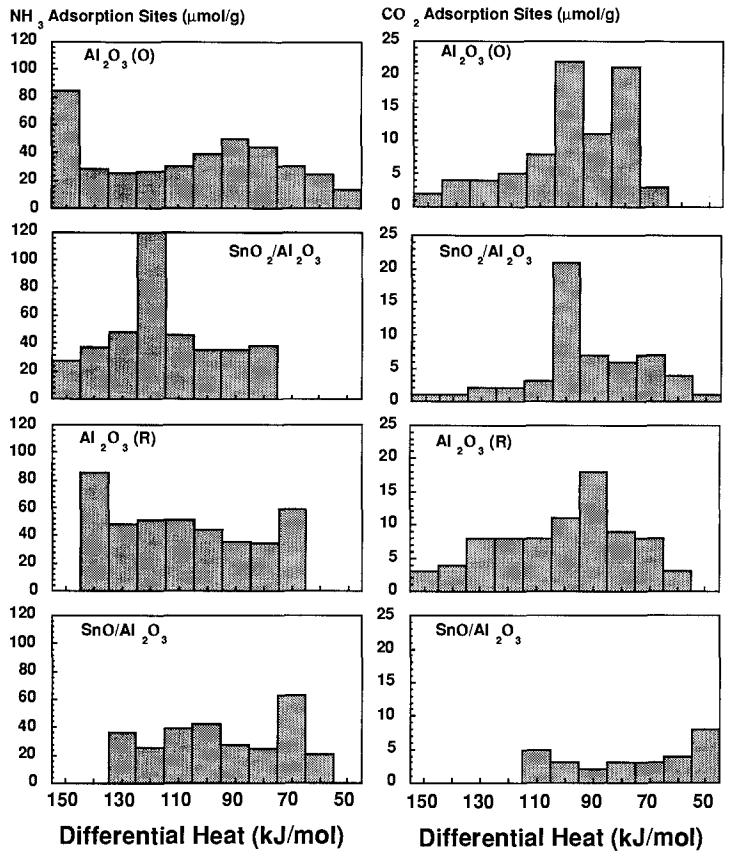

Fig. 4. Histograms of the apparent distribution of site strengths for NH_3 and CO_2 adsorption on γ-Al_2O_3, SnO_2/γ-Al_2O_3 and SnO/γ-Al_2O_3.

120 kJ/mol. Treatment of alumina in H_2 at 753 K eliminated sites with differential heat near 150 kJ/mol and slightly narrowed the site distribution. The presence of SnO eliminated sites with differential heat higher than 140 kJ/mol and significantly decreased the number of sites with heats higher than 70 kJ/mol.

The histograms of fig. 4 for CO_2 adsorption indicate that basic sites of γ-Al_2O_3 show differential heats from 70 to 150 kJ/mol. The addition of SnO_2 significantly decreased the number of CO_2 adsorption sites over the entire range of heats; however, a considerable number of sites remained near 100 kJ/mol. Treatment of γ-Al_2O_3 in H_2 at 753 K had little effect on the basic sites. The SnO/Al_2O_3 sample possessed very few basic sites, and the sites present showed differential heats lower than 110 kJ/mol.

Fig. 5 shows IR spectra collected after exposure of γ-Al_2O_3, SnO_2/Al_2O_3, and SnO/Al_2O_3 to ammonia at 423 K. The bands at 1620 and 1245 cm^{-1} for the spectrum of NH_3 on γ-Al_2O_3 can be assigned to asymmetric and symmetric deformations, respectively, of NH_3 coordinated to aluminum cations, revealing Lewis acid

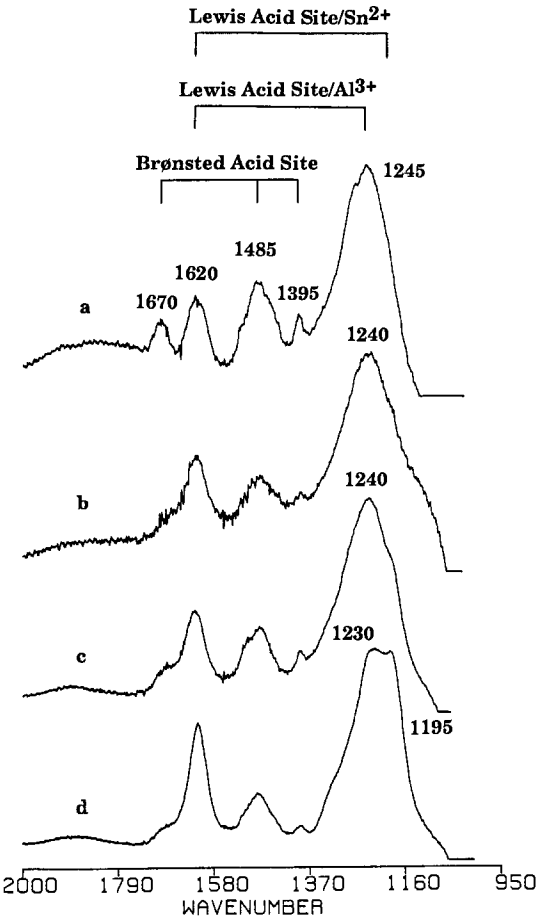

Fig. 5. Infrared spectra for ammonia adsorption at 423 K and subsequent evacuation at 298 K on γ-Al_2O_3(O) (a), SnO_2/γ-Al_2O_3 (b), γ-Al_2O_3(R) (c) and SnO/γ-Al_2O_3 (d).

sites [15,16]. The bands at 1700, 1485 and 1395 cm^{-1} are attributed to NH_4^+ species formed by the interaction of NH_3 with Brønsted acid sites [15,16]. The SnO_2/Al_2O_3 sample shows a similar IR spectrum to that of γ-Al_2O_3, except that the relative intensities of the bands due to NH_4^+ species have decreased. Treatment of γ-Al_2O_3 in H_2 at 753 K also decreased the intensities of the bands for NH_4^+ species, indicating that this thermal treatment decreased by the number of Brønsted acid sites. The presence of SnO on the γ-Al_2O_3 had the three following effects on the IR spectrum of adsorbed ammonia: (i) the relative intensity of the bands due to NH_4^+ species decreased significantly, (ii) the band due to NH_3 coordinated to Lewis acid sties shifted from 1425 to 1230 cm^{-1}, and (iii) a new band appeared at 1195 cm^{-1}.

The above IR results reveal a strong interaction between SnO and γ-Al_2O_3. Davydov showed that the symmetric band of coordinately adsorbed NH_3 is sensitive to the environment of the cations forming the Lewis acid site [16]. Specifically,

the frequency of this band increases with an increase in the valence of the cations. For SnO_2, this band appears in the range of 1240–1250 cm^{-1}, which is in the same range as for γ-Al_2O_3. This similarity explains why the IR spectrum of SnO_2/Al_2O_3 was similar to that of γ-Al_2O_3. Davydov et al. [16] found that the symmetric band of coordinately adsorbed NH_3 was in the range of 1240–1255 cm^{-1} on oxidized Sn–Mo–O and Sn–V–O catalysts, similar to the range over SnO_2. For a reduced sample with Sn/Mo = 9 : 1, they found two frequencies at 1210 and 1190 cm^{-1}. Therefore, we assign the band at 1230 cm^{-1} for the SnO/Al_2O_3 sample to NH_3 coordinately adsorbed on aluminum cations, and the band at 1195 cm^{-1} may be attributed to NH_3 coordinately adsorbed on Sn^{2+} cations. The aluminum cations involved in this Lewis acid site appear to be interacting with the Sn^{2+} cations, since the frequency of the band (1230 cm^{-1}) was significantly lower than that for γ-Al_2O_3 (1245 cm^{-1}). The shift of this band to lower frequency suggests a decrease of partial charges on aluminum cations caused by the interaction with Sn^{2+} cations, thereby decreasing the strength of Lewis acid sites. This conclusion is consistent with the microcalorimetric results of ammonia adsorption. The IR spectra for ammonia adsorption on the SnO/γ-Al_2O_3 sample after evacuation at 373 and 473 K support the assignments. Specifically, the intensity of the band near 1195 cm^{-1} decreased faster than the band near 1230 cm^{-1} upon heating in vacuum, indicating that the Lewis acid sites associated with Sn^{2+} cations were weaker than those associated with aluminum cations.

Fig. 6 shows IR spectra collected after exposure of γ-Al_2O_3, SnO_2/Al_2O_3, and SnO/Al_2O_3 to carbon dioxide at 423 K. The spectra for CO_2 on Al_2O_3 and SnO_2/Al_2O_3 were very similar. The bands near 1650, 1480 and 1235 cm^{-1} are due to bicarbonate species formed by the adsorption of CO_2 on hydroxyl groups [17,18], and bands near 1460 and 1090 cm^{-1} may be assigned to free carbonate ions [17–19]. Thornton et al. studied CO_2 adsorption on SnO_2 with IR spectroscopy and also observed the formation of carbonate and bicarbonate species [20]. Fig. 7 shows that all these bands are essentially eliminated on the SnO/Al_2O_3 sample, in agreement with the microcalorimetric result.

Bacaud et al. [6] also observed that addition of tin poisoned the stronger acidic sites of alumina. Over a catalyst with 0.47 wt% Pt and 0.47 wt% Sn (comparable to industrial Pt/Sn reforming catalysts), these authors observed that the addition of tin decreased the cracking activity of *n*-heptane at 673 K. Mössbauer spectroscopic studies indicated the presence of stannic and stannous cations associated with the alumina support, as well as Pt/Sn alloy species, and these authors attributed the decreased cracking activity to the elimination by tin species of the stronger acid sites on alumina.

Figs. 7 and 8 give comparisons of the effects on the acid/base properties of adding SnO_2 and SnO to γ-Al_2O_3 with data presented elsewhere for the effects of adding K_2O, MgO and La_2O_3 [13]. It can be seen in fig. 7 that the effect of SnO on the acidity of γ-Al_2O_3 was similar to that of MgO at low ammonia coverage. At higher ammonia coverages, the differential heat of ammonia adsorption on the sample

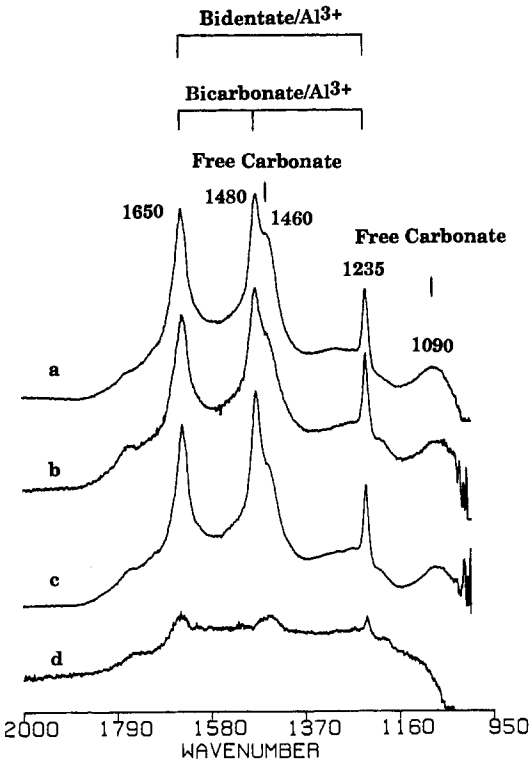

Fig. 6. Infrared spectra for carbon dioxide adsorption at 423 K and subsequent evacuation at 298 K on γ-Al_2O_3 (O) (a), SnO/γ-Al_2O_3 (b), γ-Al_2O_3 (R) (c) and SnO/γ-Al_2O_3 (d).

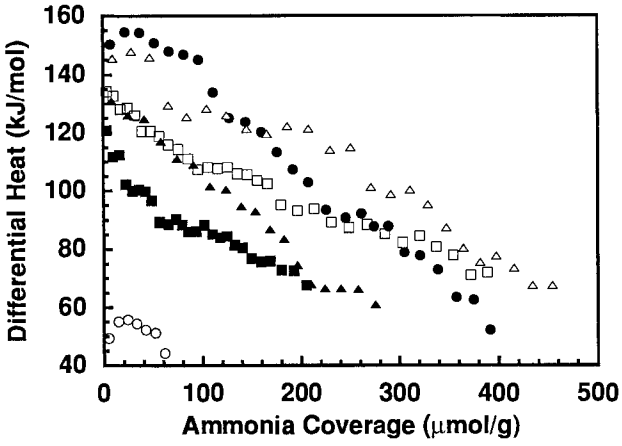

Fig. 7. Differential heat versus adsorbate coverage for adsorption of NH_3 at 423 K on γ-Al_2O_3 (●) and γ-Al_2O_3 containing oxides of 3000 μmol K^+/g (○), 3000 μmol Mg^{2+}/g (□), 3000 μmol La^{3+}/g (■), 1000 μmol Sn^{2+}/g (▲), and 1000 μmol Sn^{4+}/g (△).

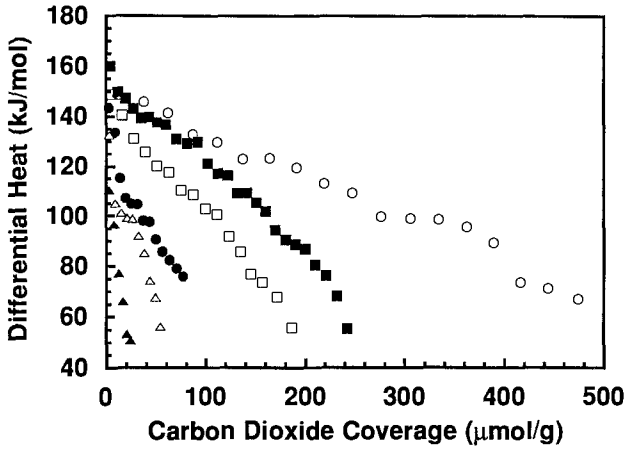

Fig. 8. Differential heat versus adsorbate coverage for adsorption of CO_2 at 423 K on γ-Al_2O_3 (●) and γ-Al_2O_3 containing oxides of 3000 μmol K^+/g (○), 3000 μmol Mg^{2+}/g (□), 3000 μmol La^{3+}/g (■), 1000 μmol Sn^{2+}/g (▲), and 1000 μmol Sn^{4+}/g (△).

containing SnO was considerably lower than that of MgO/Al_2O_3. Thus, it appears that SnO is more effective in eliminating acid sites on γ-Al_2O_3 than is MgO. It can be seen in fig. 8 that all the basic metal oxides increased the basicity of γ-Al_2O_3. In contrast, the presence of SnO decreased the basicity of the support. Thus, SnO is the most effective oxide of those that we have studied for neutralization of the acid/base properties of γ-Al_2O_3. Moreover, this system offers the unique ability to restore most of the acid and base sites on γ-Al_2O_3 by oxidizing the SnO to SnO_2.

We noted in our previous study of K_2O, MgO, and La_2O_3 on γ-Al_2O_3 that the electronegativities of these oxides could be used to correlate the effects of these oxides on the surface acid/base properties [13]. In particular, oxides with lower electronegativities were more effective in neutralizing acid sites of alumina and generating new basic sites. We may now attempt to correlate the results in figs. 7 and 8 by ranking the oxides in the following order of decreasing electronegativity:

$$SnO_2(2.89) > Al_2O_3(2.50) > SnO(2.34) > MgO(2.21) > La_2O_3(2.04) > K_2O(1.24),$$

where the Sanderson electronegativities of the oxides are given in parentheses [21]. This ranking is in agreement with the result that SnO_2 does not significantly alter the acidity of Al_2O_3, whereas SnO decreases the acidity of Al_2O_3 in a manner similar to the effect of MgO. This ranking of oxides is also consistent with the observation that SnO_2 decreases the basicity of Al_2O_3; however, it does not explain the fact that SnO is even more effective than SnO_2 in decreasing the basicity of Al_2O_3. We may suggest in this case that the Sn–O bond is stronger in the reduced oxide, thereby decreasing the availability of oxygen to bond with CO_2. Thus, it appears that oxidation state as well as electronegativity may be important in controlling the surface acid/base properties.

4. Conclusion

The additions of SnO_2 and SnO to γ-Al_2O_3 have significantly different effects on the surface acid/base properties. Specifically, SnO_2 decreases the number of strong acid sites, increases the number of weaker acid sites, and has little effect on types of acid and base sites. However, the presence of SnO on γ-Al_2O_3 caused a considerable decrease in the strength and number of acid sites, weakened Lewis acid sites associated with aluminum cations, and eliminated the basicity of the support. Thus, SnO is effective for neutralization of the acid/base properties of γ-Al_2O_3, this system offers the unique ability to restore most of the acid and base sites on γ-Al_2O_3 by oxidizing the SnO to SnO_2.

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