ACIDITY AND SURFACE BEHAVIOUR OF ALUMINA-BORIA CATALYSTS STUDIED BY ADSORPTION MICROCALORIMETRY OF PROBE MOLECULES

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Acidity and basicity of alumina-boria catalysts supported on porous or non-porous alumina have been studied by adsorption microcalorimetry of probe molecules (ammonia, pyridine and sulphur dioxide). Despite decreasing in initial heats, the total acidity as determined by ammonia adsorption increased in number and strength as a function of percentage of boron oxide. Ammonia, as a strong base, was shown to cover all types sites from strong to weak acid sites. Pyridine, as a weaker probe, was shown to dose only the stronger sites of the samples which stay nearly constant after B_2O_3 coverage approaching the monolayer. The basic sites of the amphoteric alumina support are neutralized by 10 wt% of boron oxide on non-porous alumina and 20 wt% of B_2O_3 on porous alumina. The catalytic activity for partial oxidation of ethane increased with acidity and reached a maximum constant value above 20 wt% of boron oxide.

Keywords: adsorption microcalorimetry, aluminia-boria catalysts, DSC, TG

Introduction

Adsorption microcalorimetry of probe molecules has been widely used for determination of surface acidity and basicity of catalysts [1–3]. This method allows characterization of the number of sites, energy distribution, differential and integral heats, and differential molar entropies. All these parameters are related to coverage of the catalyst surface by the adsorbed molecules. Different probe molecules can be used: ammonia and pyridine for the determination of the acid sites and sulphur dioxide for the determination of the basic sites.

To our knowledge, this type of characterization has not yet been applied to alumina-boria catalysts used in the partial oxidation of ethane [4]. The study of the acid-base behaviour is also very important for determining the mechanism of

the catalytic reaction, since these catalysts are characterized by a lack of redox property [5]. This simultaneous TG-DSC investigation was undertaken to determine the thermal stability and water content of these new catalysts.

Materials and methods

Samples

Alumina–boria catalysts with various percentages of boron oxide (10, 20, 30 wt%) were prepared by impregnation of porous (Rhône-Poulenc) and nonporous (Degussa) alumina, from a solution of boric acid (Merck). After dehydration, the catalysts were calcined for four hours in air at 873 K. After calcination, atomic absorption spectroscopy and atomic plasma emission spectroscopy were used for chemical analysis of the samples.

Surface area of the catalysts were determined by the BET method from N_2 adsorption and desorption isotherms.

Physico-chemical data are summarized in Table 1.

Table 1 Physico-chemical properties of the samples

Samples	B_2O_3 / wt%		Surface area / m^2g^{-1}	H_2O / wt% loss 773 K
	Theoretical	Chem. anal.		
Porous alumina				
	0	0	325	8
	10	9	287	10
	20	19	192	12
	30	29	70	14
Non-porous alumina				
	0	0	103	6
	10	11	105	6
	20	18	100	13
	30	25	58	13
–	100	–	0.4	–

Simultaneous TG-DSC

Differential scanning calorimetry (DSC) and thermogravimetry (TG) experiments were used for thermal stability and water content determinations. These ex-

periments were performed on the same known amount of sample in a simultaneous Setaram TG-DSC 111 under air flow (30 ml/min) and at 5 deg·min^{-1} from ambient to 873 K.

Adsorption calorimetry

Heats of adsorption of the probe molecules were measured using a heat-flow microcalorimeter of the Tian-Calvet type (Setaram C80) maintained at 353 K, linked to a glass volumetric line which allows introduction of successive small doses of gas or vapour. The equilibrium pressure relative to each adsorbed amount was measured by means of a differential pressure gauge (Datametrics). Successive doses were introduced on the samples until a final equilibrium pressure of 133 Pa was obtained. Both calorimetric and volumetric data were stored and analysed with the aid of a microcomputer.

Probe molecules

Three different probe molecules were used: ammonia ($pK_a = 9.24$, from Air Liquide) and pyridine ($pK_a = 9.24$, from Aldrich) as basic probes, sulphur dioxide ($pK_a = 9.24$, from Air Liquide) as an acid probe. All the probe molecules used were of analytical grade >99.5 purity. Ammonia was dried on sodium wires and all the probes were submitted to successive freeze–thaw pumping cycles and stored on zeolites.

Results

Assuming that a B_2O_3 molecule can be represented as a 17 Å diameter sphere, it was possible to calculate the quantity of boron oxide theoretically required to form a monolayer on porous and non-porous alumina [6–7]. This amount is around 21 wt% of B_2O_3 for porous alumina and 7 wt% B_2O_3 for non-porous samples, which means that samples prepared on non-porous alumina with 20 wt% of boron oxide content can show only B_2O_3 on their surface and that porous alumina can be partially uncovered under 20 wt% B_2O_3.

Thermal behaviour

From Table 1, it can be seen that all the samples are hydrated. Dehydration is an endothermic process and the thermal curves appeared to be highly dependent on the amount of boron oxide [8]. Following this thermal behaviour study, the samples were all calcined at 873 K and activated under vacuum (ca 10^{-3} Pa) overnight at 773 K before any calorimetry or BET experiments, as these temperatures were considered high enough to ensure complete dehydration without any weight loss of B_2O_3 by vaporization.

Acidity

Acidity studies have been performed by means of a strong base: ammonia and a weaker one, pyridine. In Fig. 1A, differential heats are plotted as a function of ammonia coverage for samples prepared with porous alumina. The initial heats corresponding to the first dose of ammonia decrease as a function of the percentage of boron oxide from $230 \, kJ \cdot mol^{-1}$ for pure alumina to $140 \, kJ \cdot mol^{-1}$ for the 30 wt% of boron oxide. The samples show much variation in shapes of differential heat curves. The volumes of ammonia irreversibly (V_{irr}) adsorbed on the surface at 353 K are given in Table 2 (from the difference between primary and secondary isotherms) and the corresponding integral heat of adsorption (Q_{int}) which represents the total heat evolved for this given adsorbed amount is also given in Table 2. The amount of ammonia required to saturate all acid sites increases gradually with boron oxide content but increases drastically with the 30 wt% B_2O_3 sample.
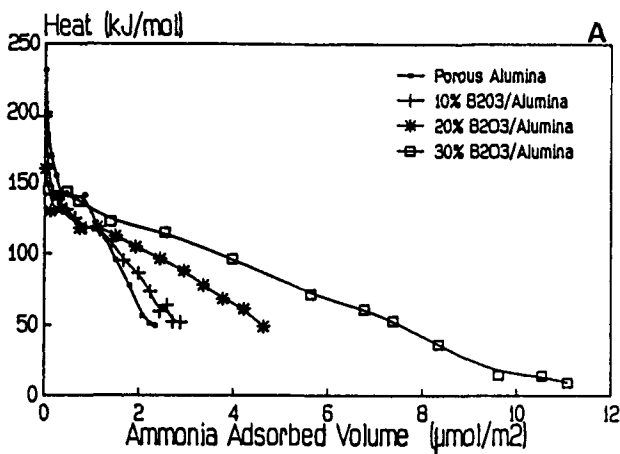

Fig. 1A Differential heat ($kJ \cdot mol^{-1}$) of adsorption of ammonia on B_2O_3/porous alumina samples *vs.* amount of adsorbed ammonia ($\mu mol \cdot m^{-2}$)

On porous alumina and 10 wt% B_2O_3 supported on alumina, a plateau corresponding to $140 \, kJ \cdot mol^{-1}$ occurs, which can be assigned to the population of active acid sites of non-covered alumina. This plateau disappears for the samples containing 20 and 30 wt% of boron oxide. For catalysts supported on non-porous alumina the initial heats for the first dose shift to lower values ($180–135 \, kJ \cdot mol^{-1}$) (Fig. 1B). Values of integral heat and volume irreversibily adsorbed are very similar to those obtained for the series prepared with porous alumina as support (Table 2).

For comparison, bulk boron oxide displays an initial heat of $80 \, kJ \cdot mol^{-1}$ and a large amount of ammonia which is irreversibly adsorbed.

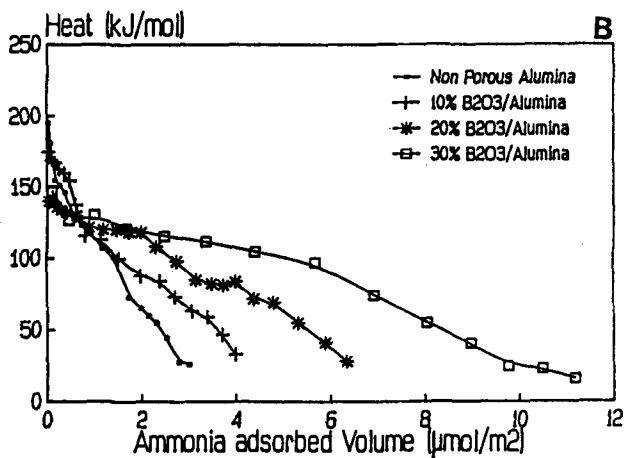Fig. 1B Differential heat (kJ·mol^{-1}) of adsorption of ammonia on B_2O_3/non-porous alumina samples vs. amount of adsorbed ammonia (μmol·m^{-2})

The differential heats of pyridine adsorption as a function of the coverage of the alumina-boria catalysts on porous alumina are given in Fig. 2A. Using this probe the initial heat and the shape of the curves do not appear to be highly dependent on the boron oxide content. The number of active sites determined by pyridine remains nearly constant on catalysts where the surface is completely covered by boron oxide (20 or 30 wt%); in contrast values obtained for pure alumina and 10 wt% B_2O_3 are lower (Table 2). Similar data are also obtained for
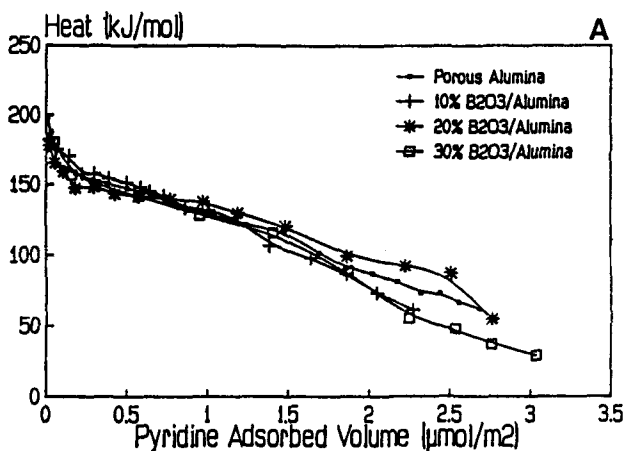

Fig. 2A Differential heat (kJ·mol^{-1}) of adsorption of pyridine on B_2O_3/-porous alumina samples vs. amount of adsorbed pyridine (μmol·m^{-2})

samples prepared on non-porous alumina (Fig. 2B and Table 2). The initial heat obtained on pure alumina $(243 \, kJ \cdot mol^{-1})$ is much higher than for any B_2O_3 catalysts and the shape of the curves varies slightly with percentage of boron oxide. On pure boron oxide the number of active sites determined by pyridine and the corresponding integral heat are much lower than those determined by using ammonia.
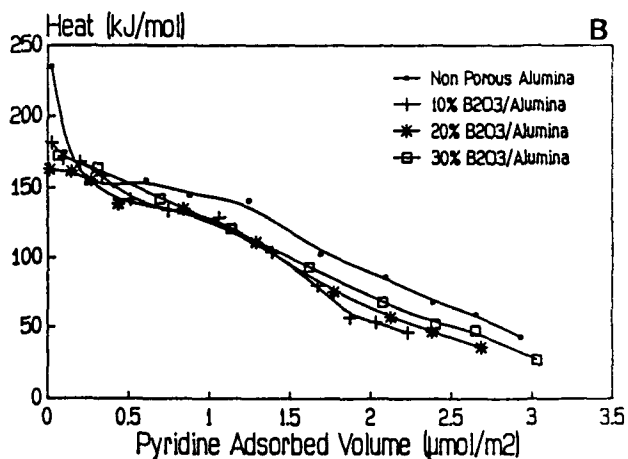

Fig. 2B Differential heat $(kJ \cdot mol^{-1})$ of adsorption of pyridine on B_2O_3/non-porous alumina samples vs. amount of adsorbed pyridine $(\mu mol \cdot m^{-2})$

Basicity

Both types of support (porous and non-porous) show high initial heats of sulphur dioxide adsorption (191 and $196 \, kJ \cdot mol^{-1}$) (Fig. 3A and 3B) and a high number of basic sites depending to the amphotericity of alumina (Table 2). On the non-porous support, with 10 wt% B_2O_3, no basic sites are observed, but some physisorption occurs. On porous alumina supported catalysts, up to 20 wt% of boron oxide is necessary before the basic sites vanish. These catalysts have been used in the partial oxidation of ethane in ethylene, and a clear correlation between acidity and ethane conversion for the partial oxidation reaction at 823 K can be observed in Fig. 4. In fact, increase of boron oxide on the alumina markedly increases the acidity of the catalysts and also its conversion capacity, up to 20 wt% B_2O_3.

Table 2 Acidity and basicity results from calorimetric adsorption data at 353 K

Samples	B_2O_3/wt%	NH$_3$		Pyridine		SO$_2$	
		V_{irr}/μmol·m^{-2}	Q_{int}/J·m^{-2}	V_{irr}/μmol·m^{-2}	Q_{int}/J·m^{-2}	V_{irr}/μmol·m^{-2}	Q_{int}/J·m^{-2}
Porous alumina							
	0	1.29	0.18	1.67	0.22	1.41	0.214
	10	1.69	0.22	1.00	0.16	0.16	0.026
	20	2.32	0.26	2.02	0.26	–	–
	30	6.55	0.69	2.02	0.26	–	–
Non-porous alumina							
	0	1.63	0.22	1.74	0.25	1.50	0.235
	10	1.83	0.23	1.41	0.19	–	–
	20	3.07	0.37	1.23	0.23	–	–
	30	5.31	0.61	1.68	0.23	–	–
	100	51.8	3.25	51.67	3.25	–	–
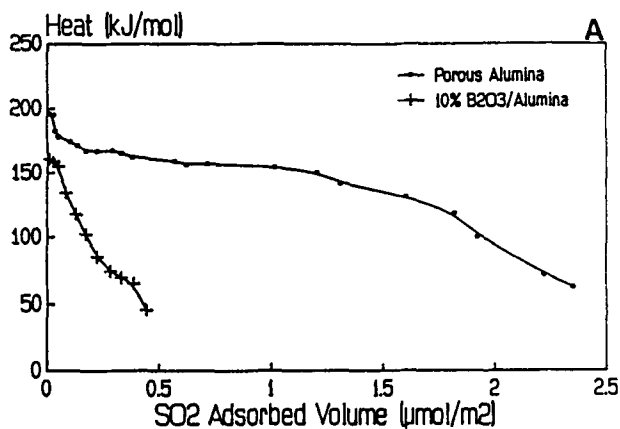
Fig. 3A Differential heat $(kJ \cdot mol^{-1})$ of adsorption of sulphur dioxide on B_2O_3/porous alumina samples $vs.$ amount of adsorbed sulphur dioxide $(\mu mol \cdot m^{-2})$
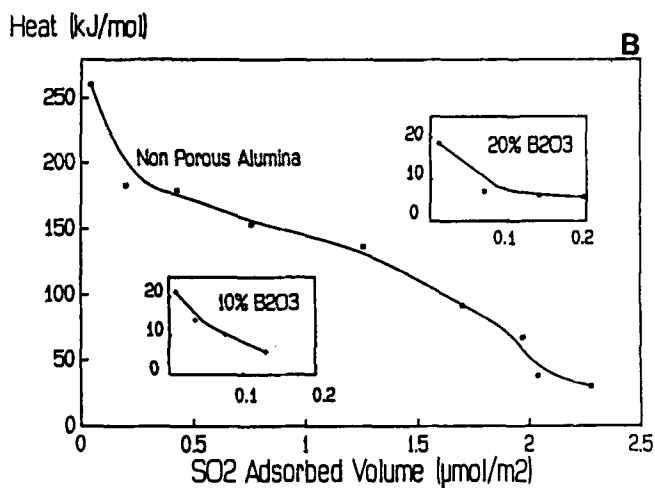

Fig. 3B Differential heat $(kJ \cdot mol^{-1})$ of adsorption of sulphur dioxide on B_2O_3/non-porous alumina samples $vs.$ amount of adsorbed sulphur dioxide $(\mu mol \cdot m^{-2})$

Conclusion

These alumina-boria catalysts reversibly adsorb water, as shown by TG-DSC [8], and under the operating conditions of the calorimetric measurements and catalytic tests, the samples are completely dehydrated and fully stable. Results of

ammonia adsorption microcalorimetry show that the two series of catalysts present a number of strong acid sites which remain nearly constant up to a concentration of 20 wt% of boron oxide; on the 30 wt% B_2O_3 sample the number of sites is much higher. The number of acid sites determined using pyridine as probe molecule remains constant whatever the quantity of boron oxide. Pyridine, perhaps because of a steric hindrance, seems to dose only a certain kind of acid sites; in comparison ammonia appears to be adsorbed at three times the volume of pyridine on the 30 wt% catalyst.
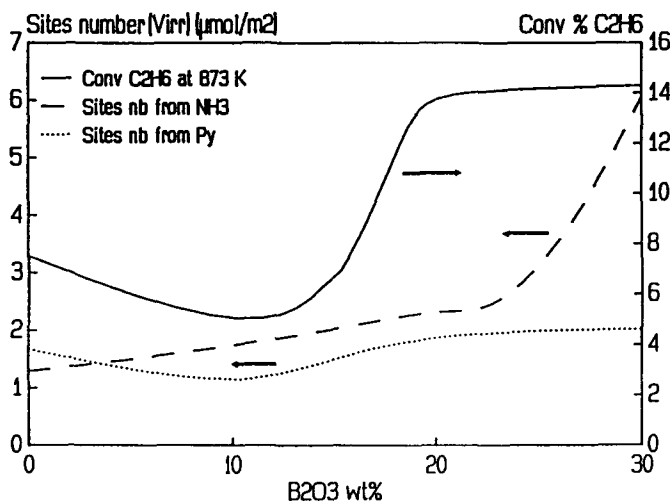
Fig. 4 Conversion of ethane (—) (%), acid strength distribution in number ($\mu mol \cdot m^{-2}$) from ammonia adsorption (– – –) and from pyridine adsorption (· · · ·) vs. B_2O_3 contents (wt%) on samples prepared on porous alumina

Heats of adsorption of pyridine for all samples are higher than for ammonia. This is due to the large differences in their pK_a values. Thus pyridine would be more accurate than ammonia for titration of the strongest acid sites of neighbouring strength. On the other hand, at the same temperature of adsorption, physisorption of pyridine is favoured by a lower vapor pressure and a higher enthalpy of vaporization. Therefore, it can be considered that chemisorption of pyridine is complete at a partial pressure much lower than 66.7 Pa which usually corresponds to the end of ammonia chemisorption.

The results clearly show that boron oxide progressively neutralizes all the basic sites of the amphoteric alumina support. The acid sites determined by pyridine adsorption follow approximately the shape of the curve of catalytic activity. Samples with 20 wt% or 30 wt% of boron oxide which show a constant catalytic activity, have also the same type and the same number of acid sites as determined by pyridine adsorption. However the large increase in ethane conver-

sion at ≥ 20 wt% B_2O_3 is not well shown on the acidity curve. The strength or strength distribution of acid sites could more probably be responsible for the catalytic activity than the number. The number of sites as determined by ammonia adsorption increases linearly with boron oxide content up to 25 wt%; the large increase at 30 wt% can be attributed to weak sites due to rearrangement of the surface close to boric acid or perborates. Similar calorimetric behaviour is observed for the sample with 30 wt% B_2O_3 and bulk boron oxide; a monolayer of highly dispersed boron oxide on the surface of the alumina appears to be mainly responsible for the high conversion and selectivity of the catalysts.

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Zusammenfassung Mittels Adsorptions-Mikrokalorimetrie von Probemolekülen (Ammoniak, Pyridin und Schwefeldioxid) wurde die Azidität und die Basizität von Aluminiumoxid-Boroxid-Katalysatoren auf porösem oder nichtporösem Aluminiumoxid-Trägermaterial untersucht. Trotz Abnahme der Anfangswärme nimmt die mittels Ammoniakadsorption ermittelte Gesamtazidität zahlenmäßig und der Stärke nach als eine Funktion des prozentuellen Gehaltes an Boroxid zu. Ammoniak deckt als starke Base alle Arten von Stellen (stark und schwach saure) ab. Das schwächere Probemolekül Pyridin deckt nur die stärkeren Probenstellen ab. Die basischen Stellen des amphoteren Trägermateriales Aluminiumoxid werden durch 10 Gew% Boroxid auf nichtporösem und durch 20 Gew% B_2O_3 auf porösem Aluminiumoxid neutralisiert. Die katalytische Aktivität für die partielle Oxidation von Ethan steigt mit der Azidität und erreicht bei 20 Gew% Boroxid einen konstanten Höchstwert.