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CALORIMETRIC STUDY OF THE ACIDITY OF ALUMINA-BORIA CATALYSTS BY GASEOUS AMMONIA ADSORPTION

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Alumina-boria catalysts were prepared by impregnation of porous and non porous aluminas with various amounts of boron oxide. A calorimetric investigation of their acidity was performed by gaseous ammonia adsorption. The differential heat evolved decreases when the amount of boria on alumina increases while the corresponding number of acid sites, as determined by volumetry, increases with the amount of boron oxide. The thermal behaviour and the stability of the catalysts, when dehydration occurs, were studied by differential scanning calorimetry linked to thermogravimetry.

Keywords: alumina-boria catalysts, calorimetry

Introduction

Several types of acid solids have been proposed as catalysts for partial oxidation of ethane such as supported V_2O_5 or MoO_3. Among those acid solids very few studies concerning alumina-boria catalysts are reported in the literature [1–8].

As it is always desirable to develop more active and selective catalysts, mainly for valorization of light alkanes, an insight in the chemistry of the B_2O_3–Al_2O_3 system appeared necessary.

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The alumina-boria catalysts are characterized by a lack of redox property, contrarily to vanadium oxide-based catalysts, which have been investigated most extensively for the partial oxidation of ethane to ethylene [9]. Since a mechanism involving a change of the oxidation state of boron cannot be involved, the role of the acidity should be dominating. To our knowledge no calorimetric studies of the acidic behaviour of supported boron oxides and bulk boron oxide have been yet performed, and adsorption microcalorimetry of probe molecules has already proved to be a powerful tool in characterizing the overall surface acidity, the number of sites and the energy distribution. This technique has previously been successfully applied to determine the energy of gas/solid interaction at the level of the interface for a series of silica, alumina and zeolites catalysts [10]. However, a few papers concerning the thermal behaviour of pure boria are reported in the literature [11, 12]. For example S. Panchout [13] has extensively described the hydration-dehydration processes of boria to boric acid and borates.

In this paper, alumina-boria catalysts were prepared with various amounts of boria. The thermal behaviour and the stability of the samples during dehydration were studied by differential scanning calorimetry and the acidity was investigated by adsorption microcalorimetry of a base probe molecule.

Experimental

Alumina-boria catalysts were prepared by an impregnation method of porous and non-porous aluminas with different solutions of boric acid; the amount of B_2O_3 was varying from 10 to 30 wt% of boron oxide. Both aluminas were gamma type. The porous alumina was SPH 557A from Rhône-Poulenc with a pore volume of 47 cm^3/100 g measured by CCl_4. Impurities determined by Chemical Analysis were: CaO 810 ppm, MgO 70 ppm, Na_2O 840 ppm, Fe_2O_3 240 ppm, SiO_2 190 ppm. Its surface area measured by nitrogen B.E.T. was 325 m^2/g. The non-porous alumina was oxide C from Degussa and the impurities were TiO_2 < 0.1 wt%, $SiO_2 < 0.1$ wt% and $Fe_2O_3 < 0.2$ wt%. The B.E.T. surface area was 103 m^2/g. The commercial boric acid was from MERCK (purity $> 99.8\%$). After filtration, the catalysts were then calcined in air at 600°C. The boron to aluminum ratio of the samples was determined from chemical analysis by atomic absorption spectroscopy (Flame N_2O/C_2H_2, $\lambda=318$ nm) and atomic plasma emission spectroscopy. The surface area of alumina-boria samples was measured by nitrogen B.E.T.. The results are listed in Table 1.

The differential heats of adsorption were determined using a heat flow microcalorimeter of Tian-Calvet type, C80 from Setaram, linked to a volumetric line which permitted the introduction of successive small pulses of reactive gas onto the samples [10]. This fitting allows simultaneously the determination of the adsorption isotherm.

Table 1 Physicochemical characteristics of the samples

Samples	B_2O_3 / wt%		Surface area /	H_2O /	NH_3 V_{irrev} /	NH_3 ΔH_{int} /
	Theoretical	Chem. anal.	m^2g^{-1}	wt% loss (500°C)	μmol / m^2	J/m^2
Alumina porous	0	0	325	8	1.29	0.18
	10	9	287	10	1.69	0.22
	20	19	192	12	2.32	0.26
	30	29	70	14	6.55	0.69
Alumina non-porous	0	0	103	6	1.63	0.22
	10	11	105	6	1.83	0.23
	20	18	100	13	2.32	0.26
	25	21	91	11	2.94	0.33
	30	25	58	13	5.31	0.61

Adsorption calorimetry experiments were performed at 80°C, in order to avoid too much interaction between physisorbed or weakly chemisorbed NH_3 with the sample and the ammonia adsorption process was carried out under a pressure not exceeding 133 Pa. Before any adsorption, the samples were evacuated overnight at 400°C and it will be shown further that this temperature is high enough to ensure a complete dehydration. Ammonia from Air Liquide (purity >99.9%) was purified by successive freeze-thaw cycles after drying on sodium wires.

The study of the dehydration was performed using a differential scanning calorimeter linked to a thermobalance (TG-DSC 111 from Setaram). The experiments were carried out in a range of temperature from 20° to 600°C at a rate of 5 $\text{deg}\cdot\text{min}^{-1}$ under a gas flow of helium.

The alumina-boria catalysts were also submitted to successive cycles of hydration and dehydration in order to study their stability and hydrophilicity. For that aim, they were successively heated to 600°C and then cooled down to 20°C four times under a gas flow of air saturated with water vapor.

Results and discussion

Thermal stability

Table 1 gives the theoretical amount of B_2O_3 deposited on alumina together with the real content as determined by chemical analysis. Assuming a molecular cross-sectional area of B_2O_3 of about 17Å^2, the calculated theoretical amount of a B_2O_3 monolayer over alumina may be evaluated respectively to 21 wt% of B_2O_3 over the porous alumina and to 7 wt% of B_2O_3 over the non porous alumina. Thus the amount of B_2O_3 over non-porous alumina is in all cases much superior to a monolayer and the active sites of alumina should be completely covered or more probably a growth of crystalline B_2O_3 occurs with formation of agglomerates.

In the case of porous alumina, B_2O_3 enters and fills easily the pore volume and this explains the large decreasing in surface area above 10 wt% with also a coincident growth of crystalline B_2O_3. For the non-porous alumina the drop of 40% in the surface area can be attributed only to the formation of large crystals of B_2O_3.

Figure 1 illustrates the thermal behaviour of the catalysts with various contents of boron oxide supported on non-porous alumina as a function of the temperature.

Dehydration is an endothermic process and the thermogram is highly depending on the amount of boron oxide. Pure alumina or with a low content of B_2O_3 (10 wt%) display a single peak which develops gradually into two peaks. Simultaneously the maxima of the peaks move towards higher temperatures.

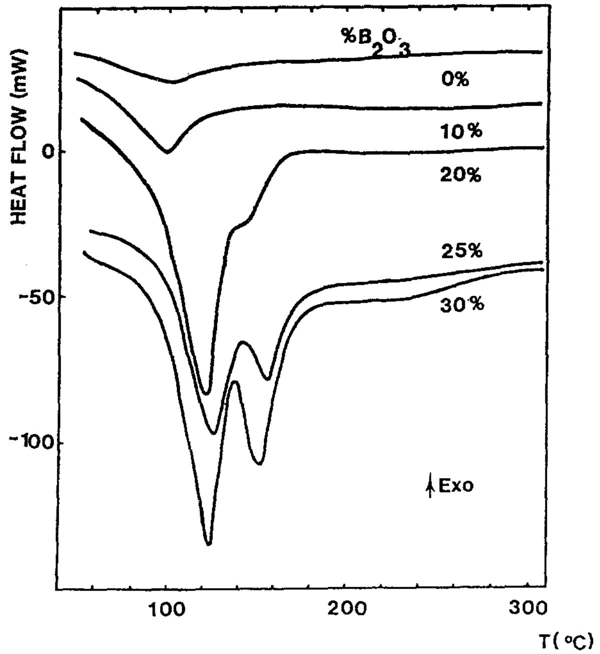

Fig. 1 Thermal study by DSC of the dehydration of boria catalysts deposited on non-porous alumina

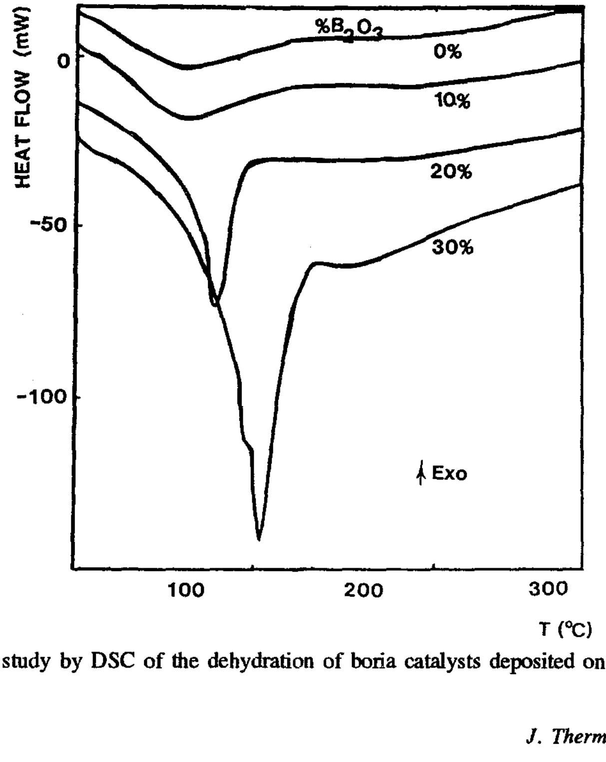

Fig. 2 Thermal study by DSC of the dehydration of boria catalysts deposited on porous alumina

The first peak can be ascribed to a loss of water physically bound to alumina, easy to remove at low temperature. The second peak can be attributed to water physically bound to boron oxide or blocked in the pore volume by steric hindrance and less easily removed. The weight loss during heating simultaneously followed by thermogravimetry is given column 4 in Table 1. No other peak was identified above 180° up to 600°C, in particular around the melting point of boron oxide (~450°C).

Figure 2 illustrates the thermal behaviour of the catalysts on porous alumina as a function of the temperature. The curves are very similar to those in Fig. 1 and can be attributed to the same phenomena.

Successive cycles of hydration-dehydration were performed on the catalyst with 20 wt% B_2O_3 on non porous alumina and no noticeable change was observed in the thermograms or in the surface area of the sample. No weight loss of B_2O_3 by vaporization or structure modification by solvatation was observed.

So the adsorption and removing of water from the samples can be considered as a reversible process.

Acidity

Figure 2 displays the differential heats of ammonia adsorption on alumina-boria catalysts on porous alumina as a function of the coverage. As it can be seen the shape of the curves is highly dependent on the boron oxide content.

The differential heat decreases progressively as the ammonia coverage increases indicating a high heterogeneity of the surface.

The initial heat, corresponding to the first dose, decreases from 230 to 145 $kJ\cdot mol^{-1}$ when the boria content increases. The progressive decrease of initial adsorption heats can be attributed to the increasing role of B_2O_3, whose behaviour at high amounts is close to bulk B_2O_3 or boric acid already known to be a weak acid. However the number of sites increases in a large proportion with boron oxide amount.

In Table 1 are reported the ammonia volume irreversibly adsorbed ($V_{irrev.}$ expressed in μmol of gas per m^2 of catalyst) on the surface at 80°C from the difference between primary and secondary isotherms and the corresponding integral heat of adsorption (ΔH_{int} expressed in J per m^2 of catalyst) which represents the total heat evolved for this given amount of ammonia.

The adsorbed volume of ammonia which represents the number of acid sites, increases exponentially with boria amount up to 20 wt%. Above 25 wt% a drastic increase of this number is observed.

On pure alumina or with a low boron ratio a plateau can be seen around 140 $kJ\cdot mol^{-1}$ which can be ascribed to a population of sites progressively removed from the alumina surface by higher coverages of boron oxide.

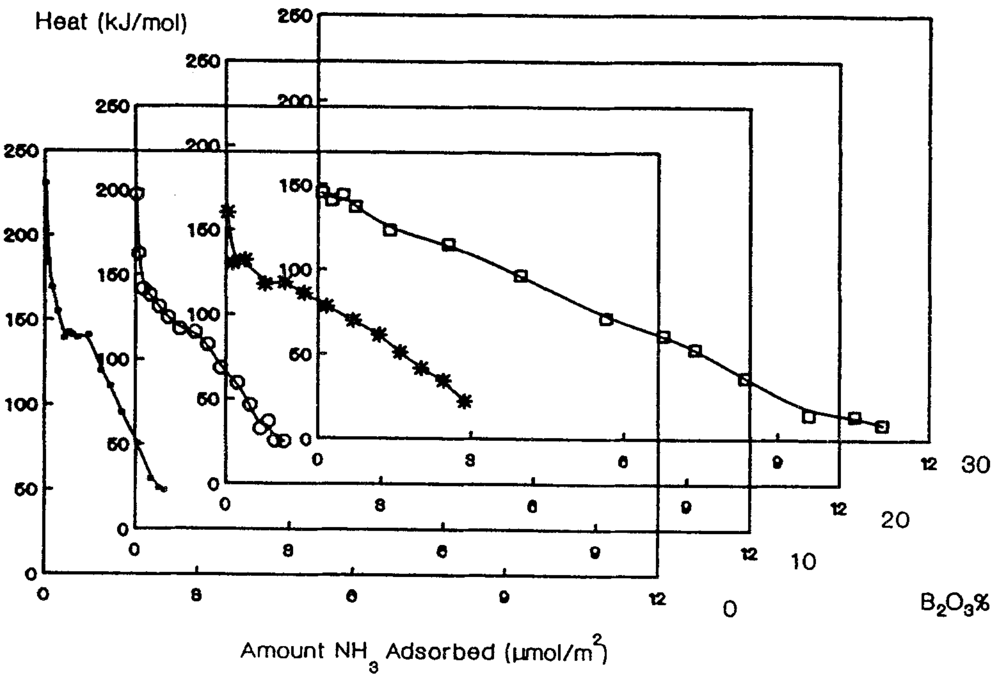

Fig. 3 Differential heat of adsorption of ammonia on B_2O_3/porous alumina samples *vs.* the amount of adsorbed ammonia

Figure 3 represents the differential heat of ammonia adsorption for the samples prepared with non porous alumina. Compared to Fig. 2 a similar behaviour was observed. The amount of acid sites increased with B_2O_3 content, however the acid strength of the first sites revealed by NH_3 is slightly shifted to lower energy. The initial heat is within 180–135 kJ·mol^{-1} which is lower than on porous alumina.

The integral heat and volume irreversibly adsorbed are very similar for the two different supports at comparable percentage of boron oxide. It can also be noticed that the differential heat curves for the pure alumina supports are very similar to those already given in the literature [10, 14] considering the lower adsorption temperatures reported.

Conclusion

The acidity of alumina-boria catalysts has been shown to increase in number (at least for the weaker sites) but not in strength with boron oxide content. Boria must generate on alumina a higher uniformity in acid property, which increases

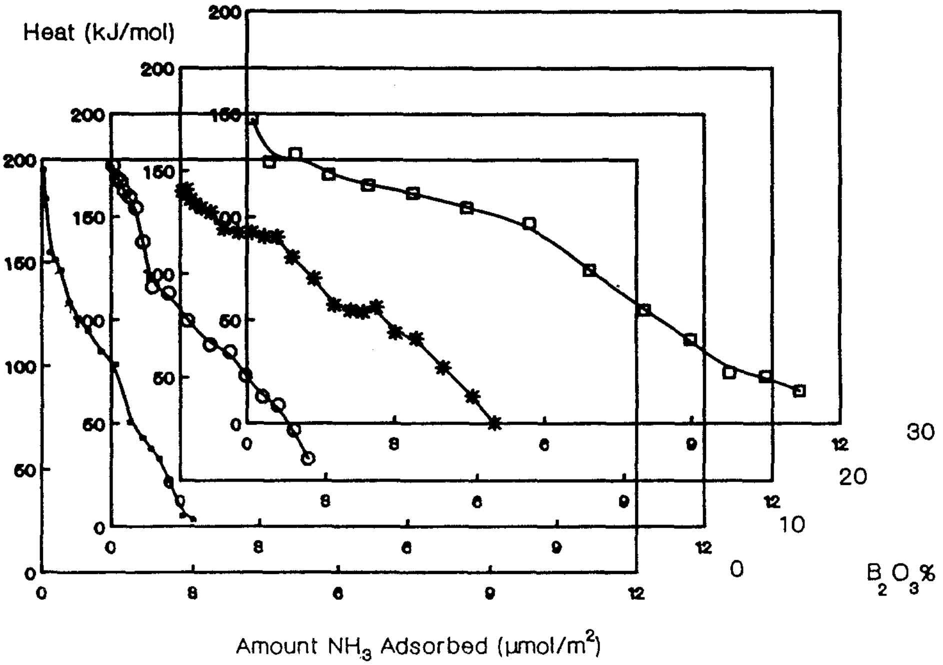

Fig. 4 Differential heat of adsorption of ammonia on B_2O_3/non porous alumina samples *vs.* the amount of adsorbed ammonia

the catalytic efficiency. From the point of view of the catalytic study, the ethane conversion increases with the amount of B_2O_3 and reaches a plateau above 20 wt% of boron oxide [15]. The results of the measurements of the differential heat of ammonia adsorption indicate that a large number of weak acid sites were created on the catalyst surface on the samples with boria amount > 20 wt% whose efficiency is not demonstrated in the catalytic process. The maximum heat values are almost the same for both series, but the average acid strength of the non porous alumina supported catalysts is greater than for the other series.

This study will help us in preparing active boria alumina catalysts which require a higher dispersion of B_2O_3 on the surface of the alumina and different optimal acid strengths to proceed effectively.

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Zusammenfassung — Mittels Imprägnierung von porösen und nichtporösen Tonerden mit verschiedenen Mengen Boroxid wurden Aluminiumoxid-Boroxid-Katalysatoren hergestellt. Durch Adsorption von gasförmigem Ammoniak wurde eine kalorimetrische Untersuchung ihrer Azidität durchgeführt. Die differentielle freigesetzte Wärme sinkt bei Zunahme der Boroxidmengen auf Tonerde, während die entsprechende Anzahl von Säurestellen mit der Menge von Boroxid zunimmt, wie durch Volummetrie festgestellt wurde.

Das thermische Verhalten und die Stabilität der Katalysatoren wurden bei Vorkommen von Dehydratation mittels DSC in Verbindung mit TG untersucht.