

## **MICROCALORIMETRIC INVESTIGATION OF THE ACIDITY AND BASICITY OF METAL OXIDES**

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The acidity and basicity of about twenty simple oxides mainly used in catalysis and ceramic materials were investigated by adsorption microcalorimetry of basic and acidic gas probe molecules such as ammonia and carbon dioxide. The determination of the number, strength and site energy distribution of both acidic and basic sites in all the samples led to an improved description of the surfaces. The results allowed us to classify our samples in three main groups in relation to their acidic, basic or amphoteric character. Their acid-base behaviour was tentatively correlated to more general electronic and redox data given in the literature such as the electronegativity.

### **Introduction**

The determination of the acidic or basic character of active sites of solid catalysts to control and predict their catalytic behaviour is of large interest.

The conversion and selectivity of a reaction are influenced not only by the nature of the active sites but also by their number and their strength.

Existing rules, valid for the acidity or basicity of solutions, appear to be only of limited value for the interpretation the acidity or basicity of solids. The determination of the differential heats evolved when known amounts of gas probe molecules are adsorbed on catalytic surfaces is a most suitable and accurate method which allows the determination of the number, strength and energy distribution of the adsorption sites [1].

So the acidic and basic characteristics of nineteen simple metal oxides were investigated by microcalorimetric measurements of the differential

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heats of adsorption of basic (ammonia) or acidic (carbon dioxide) gas probe molecules as a function of coverage.

The aim of the present work was also to seek for correlations between the acid-base properties, the heats evolved and the catalytic behaviour of these oxides for providing a thermodynamic scale of surface acidity.

We will also explore the possibility of extrapolating these results to predict heats of adsorption or number of active sites for other solids.

## Experimental

Differential heats of adsorbate adsorption were measured using a Setaram heat flow microcalorimeter connected to a vacuum and gas line equipped with a Barocel type pressure gauge to maintain the gas pressure within the range 0–200 Pa as described elsewhere [2]. The samples were pretreated overnight at 673 K under oxygen and then outgassed for 2 hours at the same temperature under vacuum of ca. 1.33 mPa.

The adsorption was carried out by introducing successive doses of known amounts of the adsorbate onto the samples. The experimental set-up was monitored by a microcomputer so that the evolved heat and the residual gas pressure could be recorded continuously following admission of each dose. Identical doses of gas were repeatedly admitted into the calorimeter cell until a final equilibrium pressure of ca. 133 Pa was reached. The calorimeter was maintained at 296 K for the adsorption of carbon monoxide and at 423 K for the adsorption of ammonia.

The probe adsorbates were carbon monoxide and ammonia from Alphagaz (purity > 99.9%). These products were purified and outgassed by freeze-jump thaw cycles and dried over molecular sieves.

Table 1

Acidic character	Cr <sub>2</sub> O <sub>3</sub>	V <sub>2</sub> O <sub>5</sub>	Nb <sub>2</sub> O <sub>5</sub>	WO <sub>3</sub>	Ta <sub>2</sub> O <sub>5</sub>	MoO <sub>3</sub>	
Surface area, m <sup>2</sup> ·g <sup>-1</sup>	39.5	271	59	37.6	22	33.5	
Amphoteric character	TiO <sub>2</sub>	ZrO <sub>2</sub>	BeO	Al <sub>2</sub> O <sub>3</sub>	Ga <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	
Surface area, m <sup>2</sup> ·g <sup>-1</sup>	120	63.3	45	124.4	21	117.5	
Basic character	ZnO	CaO	MgO	Pr <sub>6</sub> O <sub>11</sub>	ThO <sub>2</sub>	Nd <sub>2</sub> O <sub>3</sub>	La <sub>2</sub> O <sub>3</sub>
Surface area, m <sup>2</sup> ·g <sup>-1</sup>	10.5	29	197	6.2	7.5	14.1	13

The oxides samples are listed in Table 1 together with their specific area measured by the BET method with nitrogen. Their classification in the table

reflects the fact that a few oxides will appear to be exclusively acidic, a few basic only, but most are amphoteric.

## Results and discussion

The simultaneous measurements of successive small amounts of gas adsorbed on the corresponding energy changes occurring during the gas-solid adsorption process are convenient to accurately represent, by stepped curves, the differential heats versus the degree of surface coverage of a solid sample [3]. From the equilibrium data of each step, we can get both the total amount of gas adsorbed at a definite equilibrium pressure ( $\sum \Delta n_{a_i} = V a$ ) and the corresponding enthalpy of adsorption ( $\sum q_i = Q_{int}$ ). The integral heat reflects the total heat evolved from the sample when contacted by given amounts of a probe adsorbate. As said above, gas probe molecules having respectively basic and acid character, namely ammonia and carbon dioxide, have been chosen for studying the acid-base behaviour of the series of metal oxides.

Figure 1 represents the integral heats of adsorption, expressed in Joule per unit weight of the adsorbent, of CO<sub>2</sub> (in the foreground) and of NH<sub>3</sub> (in the background) for all the studied oxides named by the symbol of the corresponding cation. The diagram is representative of the adsorption strength of the active sites after the sample surfaces have been covered with 66.6 Pa of ammonia or carbon dioxide respectively. The change of the integral heats of adsorption with oxides pictures quite well the varying reactivity of the probe adsorbate molecules with respect to a given adsorbent.

This can reflect both a different number of active sites at the surface of the samples and the different strength of the adsorbate-adsorbent interactions. Spectroscopic data from literature help in characterizing the nature of the adsorbed species and make possible a better interpretation of the calorimetric results [3].

Figure 1 evidences the classification of the studied metal oxides in three main groups which are respectively acidic, amphoteric and basic. The acidic samples (Cr<sub>2</sub>O<sub>3</sub>, V<sub>2</sub>O<sub>5</sub>, WO<sub>3</sub>, Ta<sub>2</sub>O<sub>5</sub> and MoO<sub>3</sub>), left hand side of diagram, reacted with ammonia but were totally inactive with carbon dioxide, as expected. The amphoteric oxides (TiO<sub>2</sub>, ZrO<sub>2</sub>, BeO, Al<sub>2</sub>O<sub>3</sub>, Ga<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>), in the middle of the figure, were able to react with both ammonia and carbon dioxide.

The basic oxides, right hand side of the figure and separating the lanthanides-actinides group Pr<sub>6</sub>O<sub>11</sub>, ThO<sub>2</sub>, Nd<sub>2</sub>O<sub>3</sub>, La<sub>2</sub>O<sub>3</sub> from the others,

ZnO, CaO and MgO, reacted with noticeable evolved heat only with carbon dioxide.

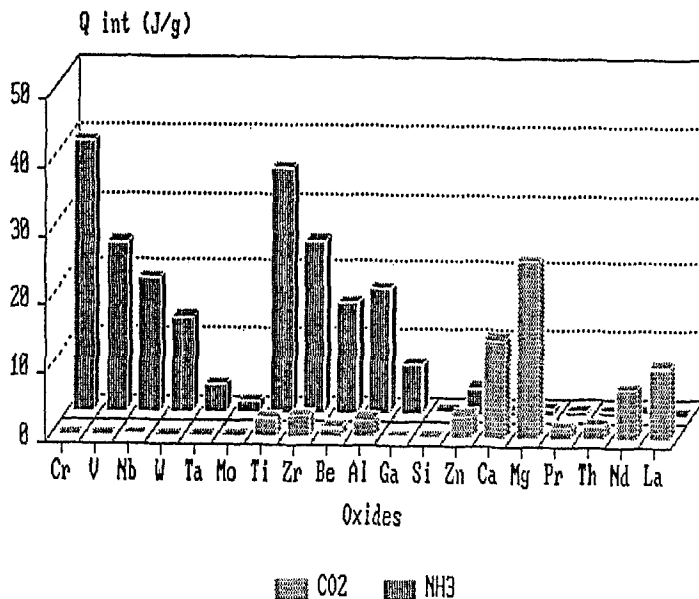


Fig. 1 Integral heats of adsorption of CO<sub>2</sub> and NH<sub>3</sub> (at the equilibrium pressure of 66.6 Pa) for all oxides

As shown Fig. 1 can be considered as providing a thermodynamic scale (or strength scale) of surface acidity and basicity over a series of simple metal oxides.

Figure 2, in a similar representation to Fig. 1, displays the amounts of carbon dioxide and ammonia adsorbed under the same equilibrium pressure of 66.6 Pa, for all samples. This diagram is representative of the number of acidic and basic sites vs. oxides and shows the same trend of classification of the oxides in three main groups. Nevertheless, this figure evidences the higher adsorption capacity of the amphoteric samples towards ammonia than carbon dioxide. For basic oxides, some ammonia adsorption occurred at pressure higher than 13 Pa, although no noticeable heat evolved was detected (see Fig. 1). This amount of ammonia adsorbed was easily removed by pumping under vacuum. Consequently it can be attributed to physical adsorption.

Besides the total values of the adsorption energies and number of sites, we present a global description of the acid-base characteristics of the

studied oxides by using three-dimensional pictures. Considering the large number of oxides, the curves relevant to all the samples were divided in two sets shown in Figs 3 and 4.

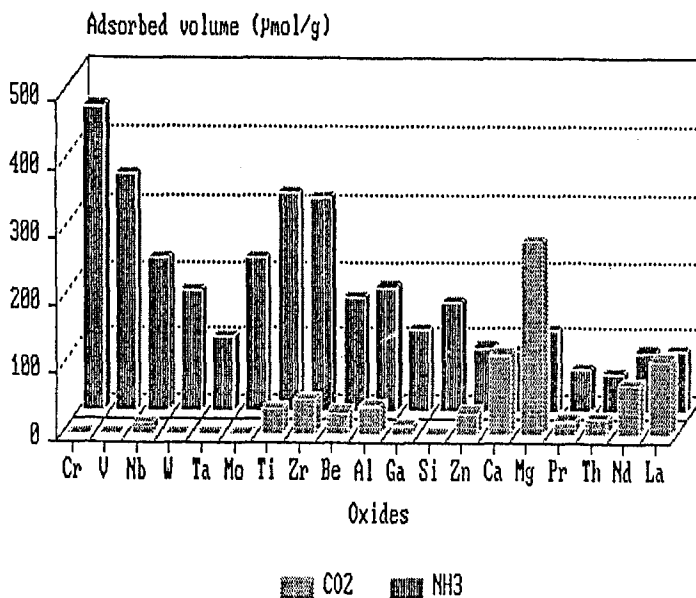


Fig. 2 Adsorbed volume of CO<sub>2</sub> and NH<sub>3</sub> (at the equilibrium pressure of 66.6 Pa) for all oxides

For a given differential heat evolved, we plotted the corresponding amounts of adsorbed ammonia and/or carbon dioxide expressed by unit surface area of the adsorbent. Each experimental point used to draw the curves refers to three axes which are the quantity of adsorbed ammonia, the quantity of adsorbed carbon dioxide and the relevant strengths of adsorption expressed by the differential heats evolved ( $\text{kJ} \cdot \text{mol}^{-1}$ ).

Samples such as the acidic ones, which reacted with ammonia only, are settled completely in the right hand side plane of the two diagrams. The basic oxides, with the lanthanides and actinides in Fig. 3 and the others in Fig. 4, which reacted noticeably with carbon dioxide only, are shown to be completely in the left hand side plane of the diagrams. The amphoteric oxides having adsorbed both ammonia and carbon dioxide with noticeable heats of adsorption are to be found in the middle of the figure planes and their corresponding experimental points are plotted in the forehead space.

For instance ZnO shows a high acidic tendency for its strong sites and a much more basic tendency for its weak sites which are prominent starting from  $100 \text{ kJ} \cdot \text{mol}^{-1}$ .

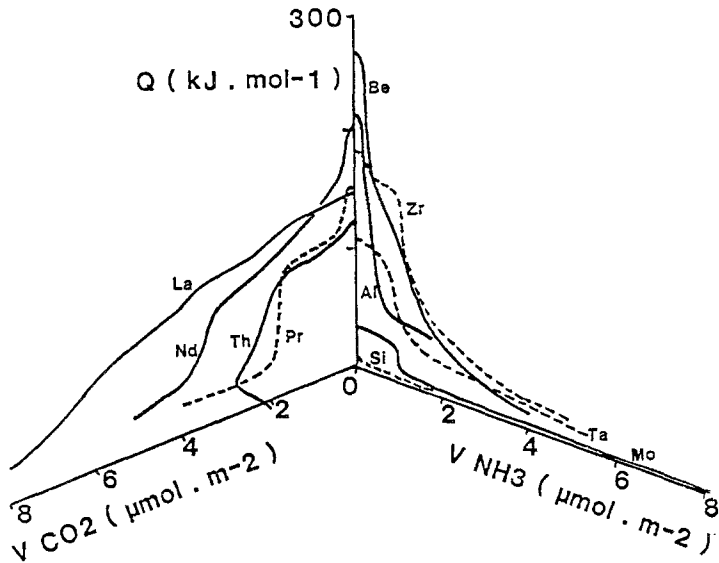


Fig. 3 Amounts of  $\text{CO}_2$  and  $\text{NH}_3$  adsorbed for a given differential heat for all samples

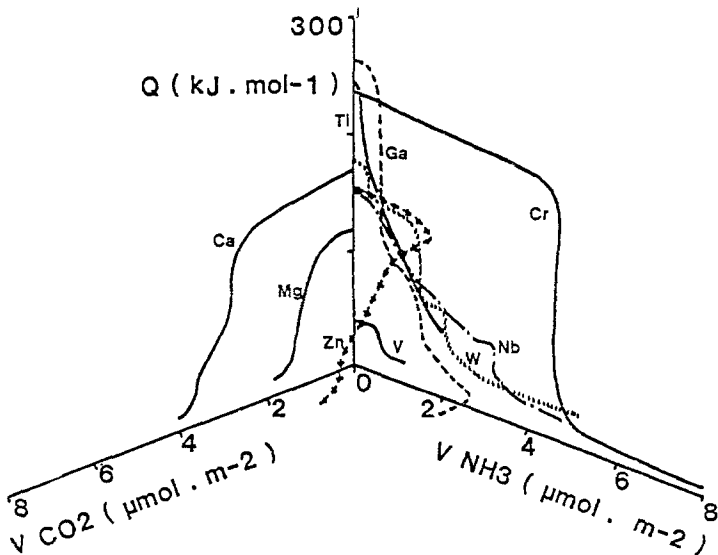


Fig. 4 Amounts of  $\text{CO}_2$  and  $\text{NH}_3$  adsorbed for a given differential heat for all samples

By contrast,  $\text{ThO}_2$  has a completely basic behaviour for its strong sites and a more acidic behaviour for its weak sites. This representation, which to our knowledge has never been previously used, permits a good visualization of the heterogeneity of the surface adsorption sites covering the overall acid-base domain of simple oxides.

Acidity and basicity are electron-accepting and electron-donating properties which can be expressed, as first approximation, by the electronegativity scale. In order to explore the possibility of extrapolating these results to predict heats of adsorption for other simple metal oxides, we have plotted the average heat of adsorption of  $\text{CO}_2$  as a function of the values of the electronegativity of the metals involved (Fig. 5).

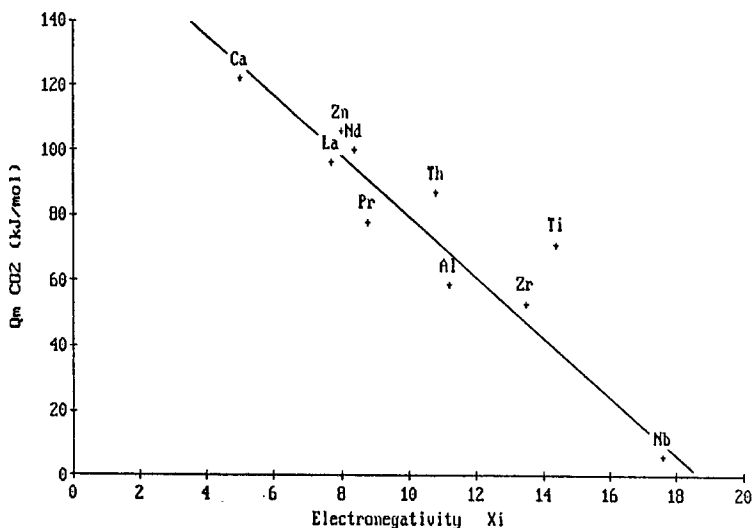


Fig. 5 Average heats of  $\text{CO}_2$  adsorption as a function of electronegativity of the metals involved

Different scales of electronegativity are reported in the literature. We selected the electronegativity values  $X_i$  from Batsanov [4] who gives a good compilation on the basis of the results obtained by different methods. This figure shows that the acid-base function would be expected to change linearly with the electronegativity of the metal ion: the larger the electronegativity, the stronger the acidic power and vice versa.

## References

1. J. Kijenski and A. Baiker, *Catalysis Today*, 5 (1989) 1.
2. A. Auroux and J. C. Védrine, in *Catalysis by Acids and Bases*, Stud. Surf. Sci. Catal., Eds. B. Imelik *et al.*, Elsevier, Amsterdam 1985, p. 311.
3. A. Auroux and A. Gervasini, *J. Phys. Chem.*, 94 (1990) 6371 and references therein.
4. S. S. Batsanov, *Russian Chem Rev.*, 37 (1968) 332.

**Zusammenfassung** – Die Azidität und Basizität von rund zwanzig vorwiegend in der Katalyse verwendeten einfachen Metalloxiden und keramischen Materialien wurden durch Adsorptions-Mikrokalorimetrie mittels basischer und saurer gasförmiger Probenmoleküle, wie Ammoniak und Kohlendioxid, bestimmt. Aus der Ermittlung der Anzahl, Stärke und Energieverteilung sowohl saurer als auch basischer Adsorptionstellen in sämtlichen Proben ergab sich eine verbesserte Beschreibung deren Oberflächen. Die Resultate erlaubten die Einteilung der untersuchten Proben in drei auf ihren sauren, basischen oder amphoterer Charakter bezogene Hauptgruppen. Das Säure-Base-Verhalten wurde versuchsweise korreliert mit allgemeineren, aus der Literatur zugänglichen Daten bezüglich elektronischer Eigenschaften und Redoxverhalten, wie beispielsweise die Elektronegativität.