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HEAT OF CHEMISORPTION OF 1-PROPANOL ON α-Al_2O_3 AT 25–200°C
A microcalorimetric study

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Abstract

We have studied by means of differential microcalorimetry the adsorption process of 1-propanol on α-Al_2O_3 at the temperatures of 25, 50, 100, 150 and 200°C, respectively. Both amounts of adsorbed alcohol and heats released decrease as the temperature of adsorption increases. At very low coverage, the high value of differential heat shows a strong irreversible chemisorption on active sites (Lewis acid sites) ($q_{diff} > 200$ kJ·mol^{-1}). Moreover, we carried out some thermokinetic investigations on heat emission peaks at different coverage degree (different equilibrium pressure of 1-propanol vapour as a function of time) and at different temperatures of adsorption, at same coverage.

Keywords: adsorption of alcohols on metal oxide surfaces, microcalorimetry, thermokinetic investigation

Introduction

The study of the adsorption of alcohols on metal oxide surfaces is of special interest in connection with catalytic decomposition of alcohols such as dehydration and dehydrogenation and with surface modification of solids for practical purposes. Many studies on the alcohols adsorption are carried out at 25°C [1, 2], but few adsorption processes are performed at temperature higher than 25°C [3]. For this reason, we have carried out the adsorption of 1-propanol on α-Al_2O_3 at different temperatures, to investigate the distribution active sites strength of alumina surface. This adsorption study at high temperature by means Calvet microcalorimeter takes part in a wide investigation of different aliphatic alcohol interactions on alumina surface.

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Experimental

a) Materials

The sample of metal oxide utilized is α-Al_2O_3 furnished by Aldrich (USA). The specific surface area of sample (15.37 $m^2 \cdot g^{-1}$) was measured by N_2 adsorption at the temperature of liquid nitrogen.

The 1-propanol is furnished by C. Erba (Milan, Italy). The alcohol, before the adsorption, was passed through a molecular sieve 3A.

b) Microcalorimetric apparatus

The microcalorimetric assembly is constituted by heat-flow microcalorimeter (Calvet type, mod. high temperature) connected to a volumetric pyrex ramp equipped with greaseless stopcocks. The measurements are carried out at 25, 50, 100, 150 and 200°C (±0.1°C). The calibration of microcalorimeter is performed by means of the Joule effect, using the standard cell of alumina with Pt resistances furnished by Setaram (Lyon, France).

The reference and laboratory cell are made of quartz, equipped with inner wall to decrease the geometrical volume, furnished by Glass-Emery (Genoa, Italy).

The microcalorimetric measurements are carried out by means of an IBM-AT computer, interfaced to the calorimeter with an A/D converter. The whole apparatus is shown elsewhere [4].

The sample of α-Al_2O_3 has been immersed in distilled water for 48 hours to have a whole hydration and then has been dried at 110°C in air. The sample, before the adsorption, is degassed under vacuum of 10^{-5} torr and at 500°C for 5 h in an oven (for elimination of physisorbed and chemisorbed water).

Results and discussion

The Figs 1 and 2 show the calorimetric and volumetric isotherms of the adsorption of 1-propanol vapour on α-Al_2O_3 for the five experimental temperatures. An increase in the adsorption temperatures always involves a decrease in both amounts and released heats. The calorimetric and volumetric isotherms appear to consist by two distinct steps. The first step represents an irreversible chemisorption, the second one represents a reversible chemisorption which is dependent by 1-propanol equilibrium pressure. All the five volumetric isotherms show the trend of Langmuir isotherm and they approximate monomolecular adsorption.

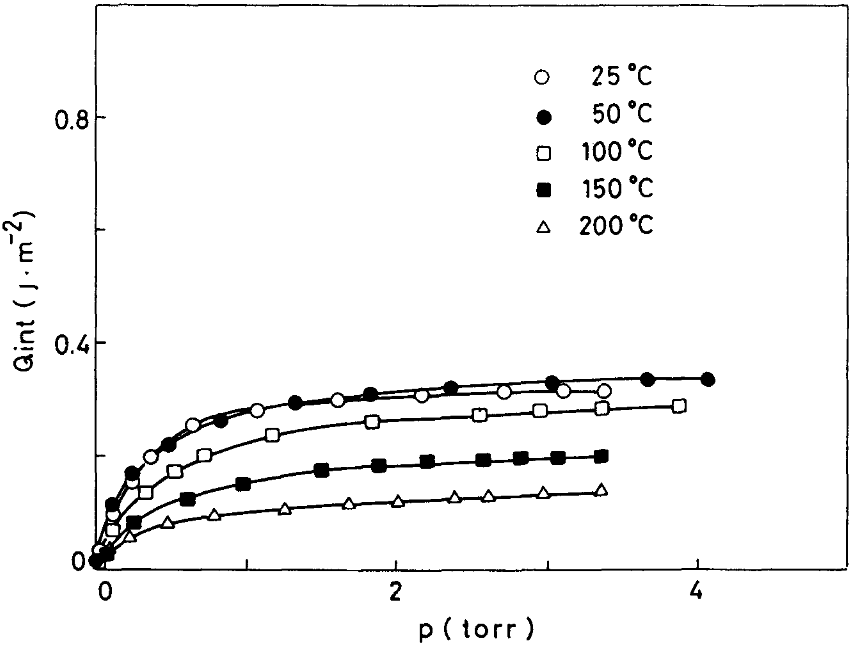
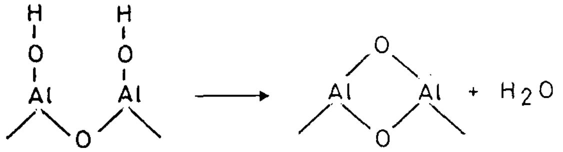
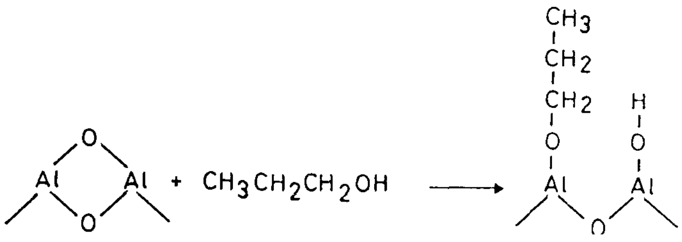


Fig. 1 Calorimetric isotherms

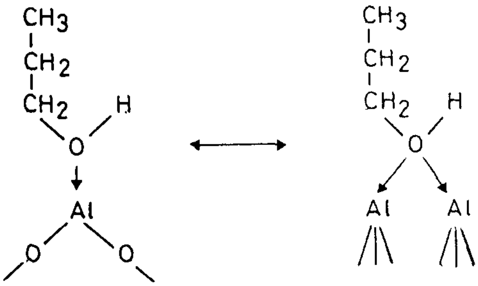
Such first data confirm the complexity of the process of chemisorption of 1-propanol vapour on α-Al_2O_3. In fact, when the sample of alumina is degassed under vacuum at 500°C, the surface hydroxyls react among them and form oxygen bridges and water according to the scheme [6]:



In contact of 1-propanol vapour, the oxygen bridges react to form the propoxy species and new surface OH groups (dissociative chemisorption), according to following reaction:



While the coordinative chemisorption of 1-propanol vapour on the aluminum cations can be presented by the following scheme:



Such adsorption mechanisms produce the irreversible and reversible adsorbed phases of 1-propanol and such balance depends on both coverage and temperature. Besides we think that at very low coverage the irreversible chemisorption is present, according to the dissociative mechanism and at relatively higher coverage, the reversible chemisorption is prevalent.

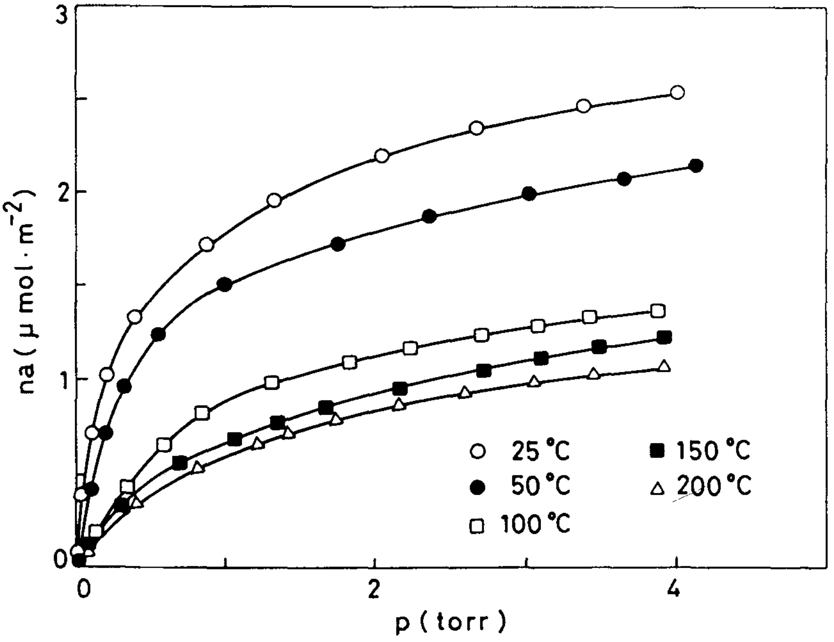


Fig. 2 Volumetric isotherms

The Fig. 3 shows the integral heats of adsorption of a μ moles adsorbed of 1-propanol vapour, for the five temperatures. From these values, we calculate for derivation, the differential heats of adsorption for the five temperatures (Fig. 4). At very low coverage, the values of differential heats for all tempera-

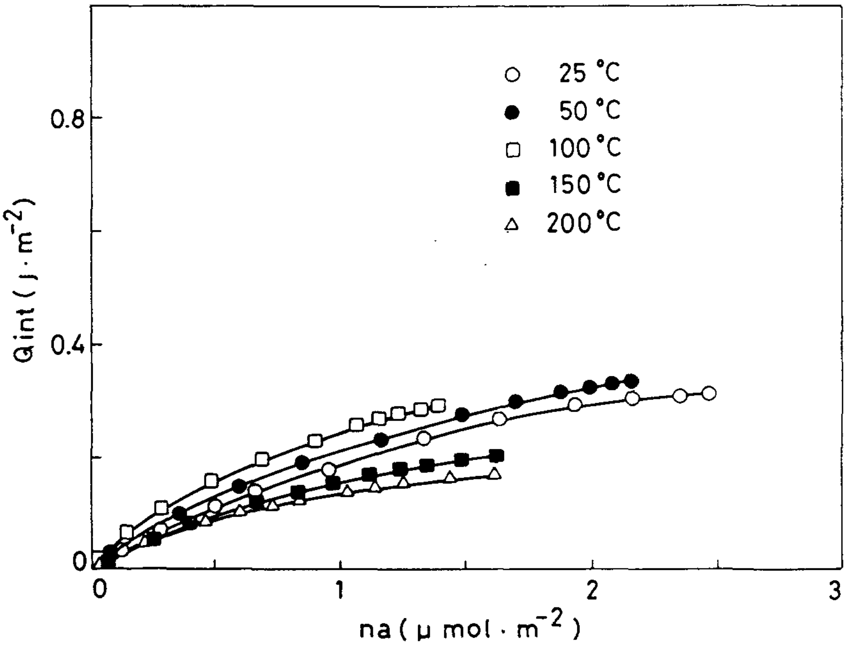


Fig. 3 Integral heats of chemisorption

tures are higher than 200 kJ·mol^{-1}. Such values appear to be independent by adsorption temperature and confirms a strong chemisorption on active sites of alumina surface (Lewis acid sites). Always in Fig. 4, the trend of differential heats are very interesting. In particular, if we consider the curves of the differential heats calculated at the temperatures of 25 and 50°C respectively, we can distinguish three regions of different active sites:

a) (qdiff > 200 kJ·mol^{-1}) an initial region of high heats representing irreversibly chemisorption on the strongest sites;

b)(200 kJ·mol^{-1} < qdiff < 70 kJ·mol^{-1}) a region of gradually declining heats representing reversibly chemisorption on intermediate sites;

c) (qdiff < 70 kJ·mol^{-1}) a region of low heats corresponding to hydrogen bonded 1-propanol.

An increase of adsorption temperature affects the trend of differential heats. In fact at the temperature of 100, 150 and 200°C, the curves of differential heats becomes steeper and they rapidly fall towards the value of hydrogen bonded 1-propanol. We think that it is possible to explain the decrease extremely rapidly of differential heats with increasing coverage and temperature. These are the extreme heterogeneity of the surface of alumina and repulsive interaction between the adsorbed molecules of 1-propanol. Both heterogeneity and repulsive interaction increase as the experimental temperature becomes higher.

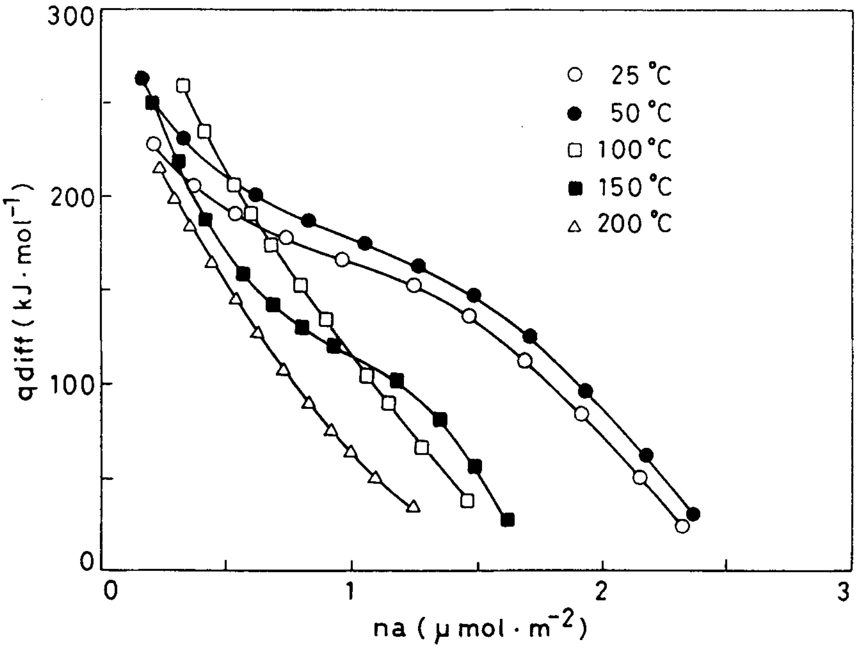


Fig. 4 Differential heats of chemisorption

Besides, the high values of differential heats, at very low coverage, are in good agreement with differential heats of methanol on α-Al_2O_3 (>200 kJ·mol^{-1}) at 200°C [5] and with those obtained by adsorption of NH_3 on γ-Al_2O_3 (>200 kJ·mol^{-1}) at 150°C [6] and with those obtained of adsorption of pyridine on Al_2O_3/SiO_2 (219 kJ·mol^{-1}) at 150°C and (214 kJ·mol^{-1}) at 200°C [7].

Thermokinetic comments

Further information on mechanism of 1-propanol adsorption on α-Al_2O_3, comes from kinetic data. As well known, heat flux curves depend on the kinetics of the process in a complex manner. Nevertheless, qualitative information may be obtained from a comparison of the heat emission peak shapes along the coverage [8]. In fact, the Fig. 5 shows some significant heat emission peaks of increasing coverage (increasing equilibrium pressure) of 1-propanol vapour at 25°C as a function of time. Each peak corresponds to admission of a single vapour dose, and therefore to a point on the calorimetric isotherms (Fig. 1). Besides also the Fig. 5 shows that the initial adsorption appears to be activated (peaks a, b, c and partially d). Heat evolution rate varies with coverage in a complex manner. Peak shape does not show a regular increase in heat emission rate with coverage for two conditions. In fact two factors appear to be in competition: the trend towards instantaneous adsorption and a variable increase in activation energy along coverage. At high coverages, when an equilibrium pressure can be more detected, the peak shape becomes close to that typical of reversible phenomena (peaks e and f). In conclusion the peaks e and f represent a fast reversible adsorption and the peaks a, b, c, and partially d, represent a very slow, clearly activated, irreversible adsorption, which is also apparent from the very slow (many minutes) decrease in the gas pressure on the adsorbent.

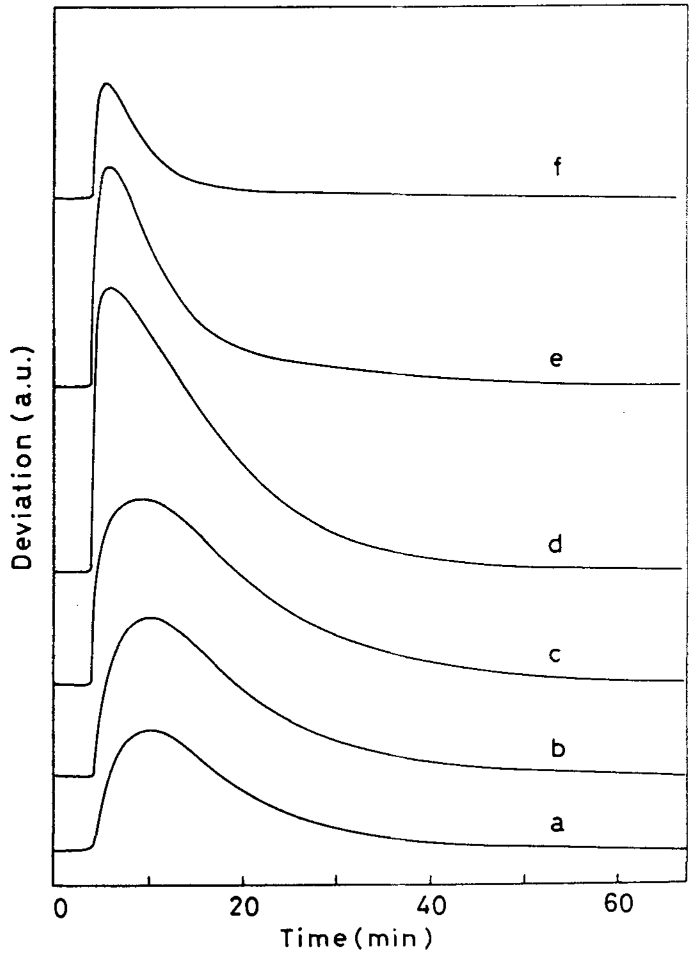


Fig. 5 Heat emission peaks as a function of 1-propanol vapour equilibrium pressure at 25°C: a) at 0.1 torr; b) at 0.3 torr; c) 0.4 torr; d) at 0.5 torr; e) at 0.9 torr; d) at 1.3 torr

At last in Fig. 6, we show five emission peaks at the same coverage degree (same equilibrium pressure) of 1-propanol vapour on alumina, but at different temperature of adsorption. The peak varies from a) to e): in fact the emission peak very rounded (a at 25°C) becomes very sharp (e at 200°C) representative of a very fast heat evolution, whose slope is of exponential type. The increase of temperature at the same equilibrium pressure treats unfairly activated irreversible adsorption and promotes very fast reversible adsorption.

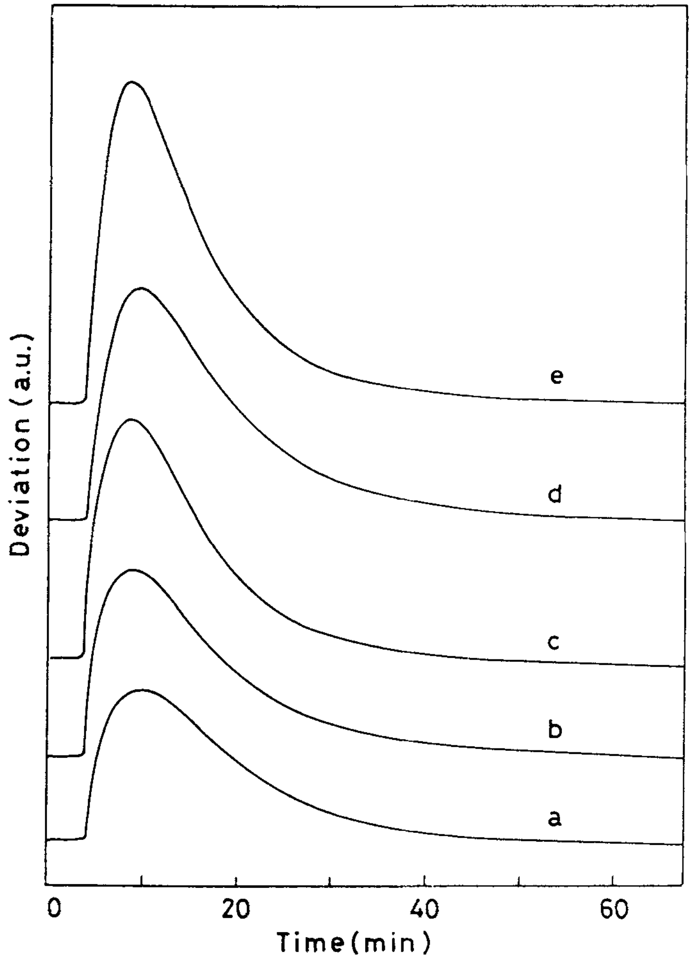


Fig. 6 Heat emission peaks as a function of adsorption temperature at the same equilibrium pressure of 1-propanol vapour (0.2 torr): a) at 25°C; b) at 50°C; c) at 100°C; d) at 150°C; e) at 200°C

Conclusions

The interaction of 1-propanol vapour on α-Al_2O_3 is a rather complex process, largely dependent upon temperature in the range 25–200°C. Moreover the adsorption of this alcohol on alumina involves the formation of various adsorbed species characterized by different heats and dependent by experimental temperature.

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Zusammenfassung — Mittels Differential-Mikrokalorimetrie wurde bei den Temperaturen 25, 50, 100, 150 und 200°C der Adsorptionsprozeß von 1-Propanol an α-Al_2O_3 untersucht. Sowohl die Menge adsorbierten Alkoholes als auch freigesetzter Wärme nimmt mit steigender Adsorptionstemperatur ab. Bei sehr geringfügiger Bedeckung zeigt der hohe Wert des Wärmeunterschiedes eine stark irreversible Chemisorption an aktiven Stellen (Lewis-Säure-Stellen) (qdiff> 200 $kJ \cdot mol^{-1}$). Weiterhin führten wir einige thermokinetische Untersuchungen des Wärmeemissionspeaks bei unterschiedlicher Bedeckung (unterschiedlicher Gleichgewichtsdruck von 1-Propanoldampf als Funktion der Zeit) sowie bei verschiedenen Temperaturen und gleicher Bedeckung durch.