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# HEATS OF CHEMISORPTION OF *n*-ALIPHATIC ALCOHOLS ON $\alpha$-$Al_2O_3$ AT 25-200°C
## A thermokinetic study

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## Abstract

A differential microcalorimeter (E. Calvet) was used to study the processes of adsorption of five aliphatic alcohols ($C_1$–$C_5$) on $\alpha$-$Al_2O_3$ at 25, 50, 100, 150 and 200°C. In particular, the importance of the thermokinetic study of the chemisorption of such alcohols at different experimental temperatures was demonstrated, with regard to the variations in the thermokinetic parameters ($t_{max}$, $t_{1/2}$ and $t_o$) and the evolution of the alcohol vapor pressure on the adsorbent during the adsorption process. It was concluded that:

a) all the heat emission peaks of alcohol adsorption have the same rounded shape at 25°C;

b) on passing from methanol to 1-pentanol, the area of the adsorption peaks increases as the chain length or molecular weight increases;

c) on passing from 25 to 200°C, the shape of the adsorption peaks becomes more pointed.

**Keywords:** adsorption of *n*-aliphatic alcohols on alumina, microcalorimetry, thermokinetic investigation

## Introduction

The adsorption of alcohols on $\alpha$-$Al_2O_3$ deserves detailed investigation, since this is a very important catalyst for the decomposition reactions of alcohols, such as dehydration and dehydrogenation. Many studies of the adsorption of alcohols on $\alpha$-$Al_2O_3$ and on different metal oxides have been carried out [1, 2] in a thermodynamic way, but not from a thermokinetic aspect.

Our present aim is to contribute to an understanding of the knowledge concerning the adsorption characteristics of *n*-aliphatic alcohols on an $\alpha$-$Al_2O_3$ surface from the aspect of the kinetic data.

## Experimental

### *Materials*

The characteristics of the alumina utilized ($\alpha$-$Al_2O_3$, 99.999%), the different alcohols and the conditions of pretreatment before adsorption were described earlier [3].

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### *Microcalorimetric apparatus*

The microcalorimetric assembly consists of a heat flow microcalorimeter (E. Calvet type, mod. high temperature) connected to a volumetric pyrex ramp equipped with greaseless stopcocks. The measurements were carried out at 25, 50, 100, 150 and 200°C (±0.1 °C) [4].

## Results and discussion

The five aliphatic alcohols used were methanol (MeOH), ethanol (EtOH), 1-propanol (1-PrOH), 1-butanol (1-BuOH) and 1-pentanol (1-PeOH).

The thermodynamic data, i.e. the calorimetric and volumetric isotherms, and the differential heats, obtained by differentiation of the integral heats of adsorption of these alcohols on $\alpha$-$Al_2O_3$, have already been published [3]. The variations in these thermodynamic parameters with the chain length or molecular weight of the alcohols are currently awaiting publication [5].

In the present work, we consider the thermokinetic parameters, i.e. $t_{max}$=time of attainment of the peak maximum, $t_{1/2}$=time of the half deviation, and $t_0$=time of return to the baseline zero (Fig. 1). The pressure of the adsorbed gas is related to the adsorption process, and consequently the final pressure or equilibrium pressure is an important thermokinetic parameter [6]. It is well known that the shape of the whole calorimetric signal is affected by the inertia of the microcalorimeter (i.e. the response time, in our case about 1800 s) [7, 8] and that very complex calculations are necessary to obtain the true thermokinetics of the studied phenomenon [9]. In our investigation, we can utilize such thermokinetic experimental data with a good approximation, because the values of the three parameters are average values. In fact, these times represent neither very slow not very fast phenomena. The response time of the microcalorimeter also affects the calorimeter signal at different temperatures.

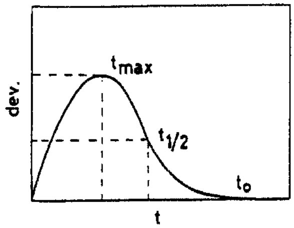

**Fig. 1** An example of heat emission peak (in evidence the different times of adsorption process)

Figure 2 depicts the five heat emission peaks of the homologous series of aliphatic alcohols at 25°C and the same equilibrium pressure (about $p_{eq.}$=0.2 torr). All the peaks have the same rounded shape, with a very slow return to the baseline zero of the recorder. The area of the peak increases with increase in the chain length or molecular weight of the alcohol.

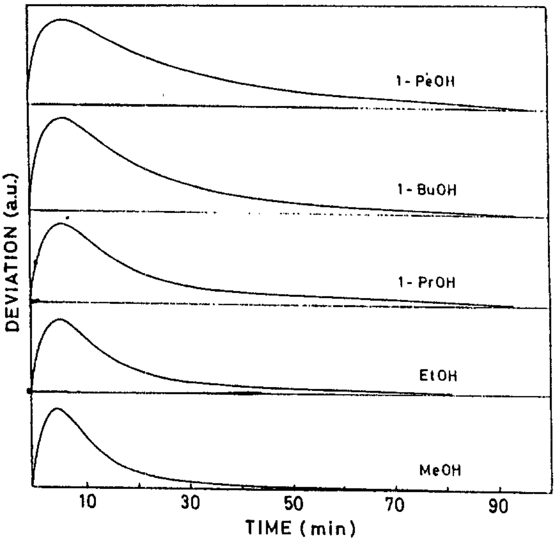

**Fig. 2** Five heat emission peaks of homologous series of aliphatic alcohols at 25°C and at $p_{eq.}=0.2$ torr

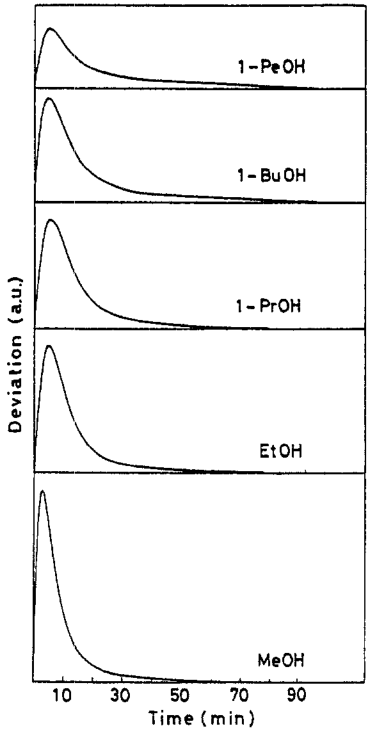

**Fig. 3** Five heat emission peaks of homologous series of aliphatic alcohols at 200°C and at $p_{eq.}=0.2$ torr

Figure 3 presents the five emission peaks at the same equilibrium pressure, but at 200°C: the shape of the heat emission peaks is clearly changed, passing from a rounded shape at 25°C to an acute shape at 200°C. Moreover, as the molecular weight increases, the sharp shape of the peak of MeOH adsorption attenuates, becoming more rounded on progression to EtOH, 1-PrOH, 1-BuOH and 1- PeOH.

For completeness, Fig. 4 illustrates the effect of temperature on $t_{max}$ for five aliphatic alcohols at the higher equilibrium pressure of 1 torr. $t_{max}$ for such adsorbed alcohols, at all temperatures, follows the sequence

$$t_{max}\,\text{MeOH} > t_{max}\,\text{EtOH} > t_{max}\,\text{1-PrOH} > t_{max}\,\text{1-BuOH} > t_{max}\,\text{1-PeOH}$$

At 50, 100 and 150°C, the heat emission peaks of the five aliphatic alcohols have an intermediate shape.

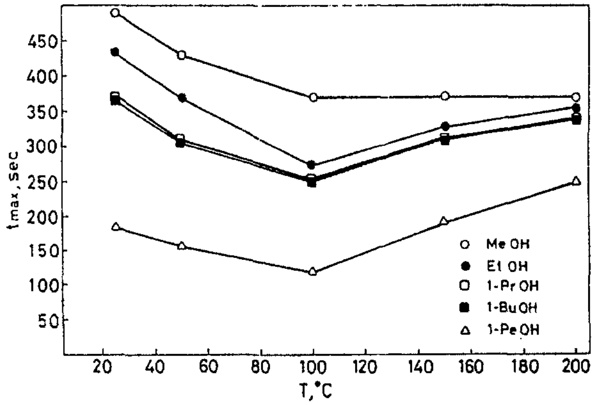

Fig. 4 Variations of the '$t_{max}$' of different aliphatic alcohols as a function of experimental temperature

The three thermokinetic parameters ($t_{max}$, $t_{1/2}$ and $t_o$) demonstrate the same tendencies in response to increasing experimental temperature and increasing number of carbon atoms in these aliphatic alcohols. $t_{max}$ is the most interesting thermokinetic parameter. Its change reflects the degree of alcohol chemisorption (activated process) on the $\alpha$-$Al_2O_3$ surface. A higher $t_{max}$ indicates greater irreversible chemisorption (activated process; heat emission peak with a very rounded shape), whereas a smaller $t_{max}$ (heat emission peak with acute shape) demonstrates a higher percentage of reversible chemisorption. In fact, as may be seen in Figs 2 and 3 from the different shapes of the heat emission peaks for MeOH at 25 and 200°C, increasing temperature more clearly reveals the higher percentage of reversible chemisorption (acute shape).

As concerns the trend of $t_{max}$ as a function of the equilibrium pressure of the adsorption process of MeOH on $\alpha$-$Al_2O_3$ at five experimental temperatures (25, 50, 100, 150 and 200°C) (Fig. 5), there is a maximum at about 1 torr, which decreases as the experimental temperature increases. The difference $t_{max}$ at different temperatures decrease very slowly to an approximately constant value of 125 s.

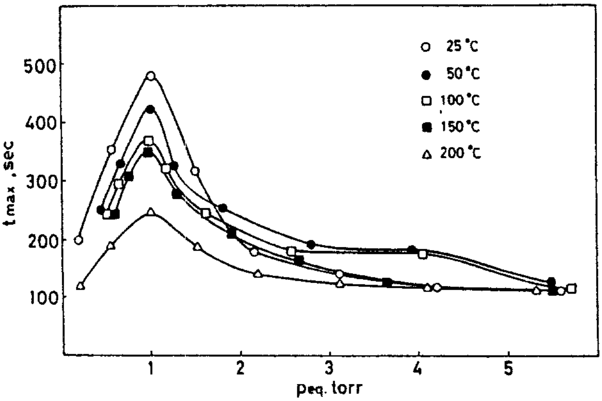

Fig. 5 Variations of the '$t_{max}$' of MeOH adsorbed on $\alpha$-$Al_2O_3$ as a function of equilibrium pressure at five experimental temperatures (25, 50, 100, 150 and 200°C)

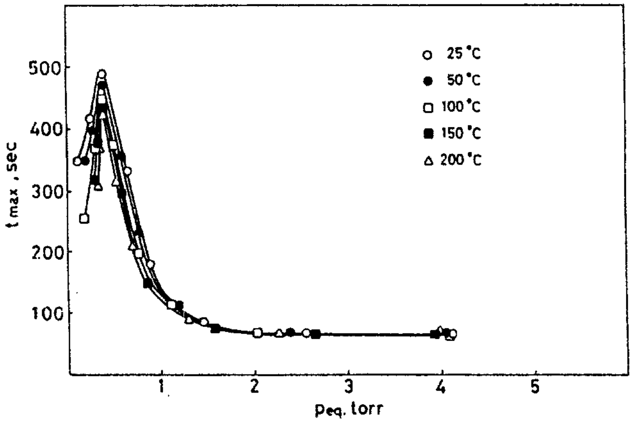

Fig. 6 Variations of the '$t_{max}$' of 1-PeOH adsorbed on $\alpha$-$Al_2O_3$ as a function of equilibrium pressure at five experimental temperatures (25, 50, 100, 150 and 200°C)

Figure 6 depicts the trends in $t_{max}$ as a function of the equilibrium pressure of the adsorption process of 1-PeOH on $\alpha$-$Al_2O_3$ at five experimental temperatures. The difference between the two graphs is very evident, for in the last graph (1-PeOH adsorption) the maximum in $t_{max}$ is shifted to about 0.4 torr. Moreover, at all temperatures, $t_{max}$ decreases very rapidly towards an almost constant time of 73 s.

The different behaviour of the two aliphatic alcohols during adsorption on the $\alpha$-$Al_2O_3$ surface can be attributed to their different cross-sectional areas or different chain lengths (i.e. steric hindrance). The shifting towards smaller values of equilibrium pressure of $t_{max}$ during the adsorption of 1-PeOH is ascribed to this being a larger molecule. In fact, in a shorter time it covers the same area of $\alpha$-$Al_2O_3$ as that covered by the smaller molecule of MeOH. This conclusion is supported by the three aliphatic alcohols displaying intermediate behaviour of $t_{max}$ as a function of equilibrium pressure at all experimental temperatures.

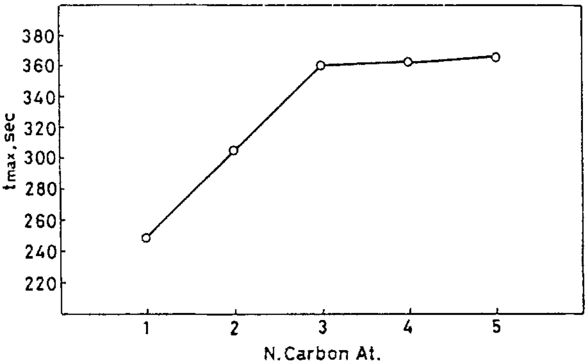

**Fig.** 7 Variations of '$t_{max}$' of different aliphatic alcohols adsorbed on α-$Al_2O_3$ as a function of number of carbon atoms (at 25°C and at $p_{eq.}$ =0.2 torr)

Figure 7 illustrates the trend of $t_{max}$ (at 25°C and $p_{eq.}$=0.2 torr) for different aliphatic alcohols as a function of the number of carbon atoms. There is an evident increase on passing from MeOH to 1-PrOH, followed by approximate constancy from 1-PrOH to 1-PeOH.

Figure 8 presents the variations in $t_{1/2}$ and $t_0$ for the five aliphatic alcohols as a function of the number of carbon atoms under the same experimental conditions. Moderate and continuous increases may be observed, again depending on the different molecular structures of these aliphatic alcohols. This monotonous increase in the thermokinetic parameters shows that the mechanism of adsorption of the aliphatic alcohols on α-$Al_2O_3$ is the same for the five alcohols at all temperatures, with the hydrocarbon chain perpendicular to the α-$Al_2O_3$ surface.

Finally, Fig. 9 demonstrates the heat emission peak of 1-BuOH adsorbed on α-$Al_2O_3$ at 100°C and at different equilibrium alcohol vapour pressures (a: 0.2 torr,

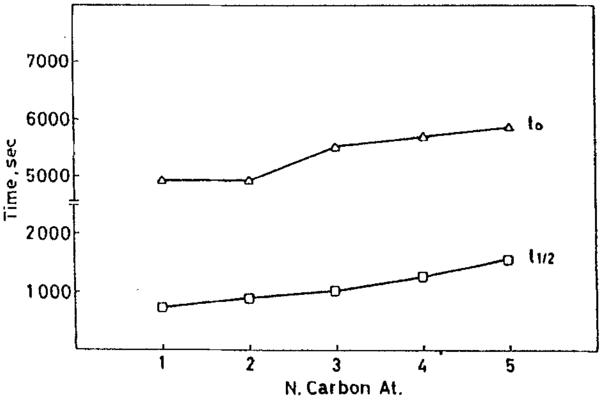

**Fig.** 8 Variations of '$t_{1/2}$' and '$t_o$' of different aliphatic alcohols adsorbed on α-$Al_2O_3$ as a function of number of carbon atoms (at 25°C and at $p_{eq.}$ =0.2 torr)

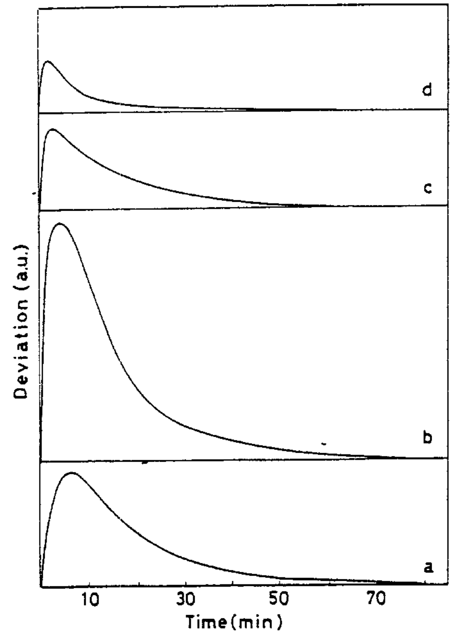

Fig. 9 Four heat emission peaks of 1-BuOH adsorbed on $\alpha$-$Al_2O_3$ at 100°C and at different equilibrium pressure ($a$=0.2 torr, $b$=0.4 torr, $c$=1.3 torr and $d$=1.6 torr)

b: 0.4 torr, c: 1.3 torr and d: 1.6 torr). At very low coverage, the adsorption process is very slow (Fig. 9a). In this case there is a connection between the kinetic and thermokinetic results, i.e. the time necessary for attainment of the adsorption equilibrium of the gas phase ($t_e$) coincides with the time of return to the baseline zero of the calorimetric peak ($t_0$). It can be concluded that the dominant kinetic process is an activated irreversible process. In contrast, in Fig. 9b the value of $t_e$ is lower than that of $t_0$ and the shape of the calorimetric peak becomes very close to that for reversible adsorption. The last predominant process can be the coordination of the undissociated alcohol.

At higher coverage (Fig. 9c and 9d), the reversible adsorption predominates and becomes ever faster with increasing alcohol vapour pressure (region of low differential heat of adsorption, near 40 kJ $mol^{-1}$, corresponding to H-bonded alcohol) [6].

The same conclusions were reached for the adsorption mechanisms of the other alcohols on the $\alpha$-$Al_2O_3$ surface at all five experimental temperatures, although with slight variations.

## Conclusions

These data confirm the complexity of the adsorption of the five aliphatic alcohols on the $\alpha$-$Al_2O_3$ surface from thermokinetic considerations. In particular, they clearly reveal the simultaneous existence of different adsorption mechanisms, leading to reversible and irreversible phases, whose balance depends on both coverages and temperatures, as some of them are activated.

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