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Variations in the chemisorption of methanol on α-Al_2O_3 in the range 200–300°C [1]

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Abstract

Using a high-temperature Calvet microcalorimeter, we have studied the chemisorption process of methanol on α-Al_2O_3 at 200, 250 and 300°C.

From the measurement of calorimetric isotherms, volumetric isotherms and chemisorption differential heats, we have demonstrated the existence of Al sites of different strengths in α-Al_2O_3. At very low coverage of methanol, such active sites ($q_{diff} > 200$ kJ mol^{-1}, Lewis sites) are very strong and methanol is irreversibly adsorbed as methoxy groups by means of a dissociative mechanism, while at medium coverage, the sites are less strong ($q_{diff} < 200$ kJ mol^{-1}) and methanol is reversibly adsorbed by means of a coordinative mechanism.

INTRODUCTION

The chemisorption of different aliphatic alcohols on metal oxides has mostly been studied to investigate the surface properties of such compounds [1, 2].

We have already studied the adsorption of methanol on δ-Al_2O_3 [3] both at room temperature and in the range 25–200°C, in order to study the different adsorbed species of methoxy groups [4].

In the present work, we have carried out a microcalorimetric study of the chemisorption of methanol vapour on α-Al_2O_3 in the 200–300°C range to investigate if methanol can be used as a molecular probe and if the distribution of adsorption strength of methanol on the active sites of alumina changes according to the experimental temperature.

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EXPERIMENTAL

Materials

The metal oxide (about 2 g) used was α-Al_2O_3 (99.999%) from Aldrich (USA).

The sample was first immersed in distilled water at room temperature for 48 h to achieve maximum hydration; then it was dried at 100°C in air.

The specific surface area of α-Al_2O_3 degassed at 500°C and in a vacuum of 10^{-5} torr, was found to be 15.37 $m^2\,g^{-1}$ on the basis of N_2 adsorption data.

The methanol was from C. Erba (Milan), and it was dried over molecular sieve 3 A.

Microcalorimetric apparatus

The microcalorimetric assembly was composed of a heat-flow microcalorimeter (high-temperature Calvet type, ±0.1°C) connected to a volumetric apparatus to evaluate the adsorption. The measurements were carried out at 200, 250 and 300°C.

The microcalorimeter calibration was performed by means of the Joule effect, using a standard alumina cell with Pt resistance (Setaram, France).

The reference cell and the laboratory cell were made of quartz, equipped with inner walls to reduce the geometrical volume (Glass-Emery, Genoa).

The microcalorimetric measurements were carried out using an IBM-AT computer, interfaced with an A/D converter. The apparatus scheme has been shown elsewhere [5].

Before the adsorption, the sample of α-Al_2O_3 was degassed under a vacuum of 10^{-5} torr at 500°C in a oven for 5 h (for elimination of the physisorbed and chemisorbed water).

After this pre-treatment, the calorimetric cell containing α-Al_2O_3 under vacuum, was inserted into the microcalorimeter at a temperature of 200°C and connected to a volumetric Pyrex-glass line for vapour adsorption. Then the first methanol adsorption up to the surface saturation of the sample was carried out (run 1).

After complete degassing of the alumina sample (at 10^{-5} torr and 200°C for 4 h) inside the microcalorimeter, we carried out a second methanol adsorption at 200°C to measure the reversible fraction of the adsorbate at the same temperature (run 2). The same process of sample pretreatment before the methanol adsorption was then carried out at the experimental temperatures of the microcalorimeter. In this way, the reversible fractions of the adsorbate were also measured at 250 and 300°C, respectively.

RESULTS AND DISCUSSION

Figures 1 and 2 show the calorimetric and volumetric isotherms for the three temperatures and for both runs.

An increase in temperature always involves a decrease in both the amount of adsorbed material and in the heat released. The first run (adsorption of methanol on the dehydroxylated surface) appears to consist of an irreversible chemisorption followed by a pressure-dependent process.

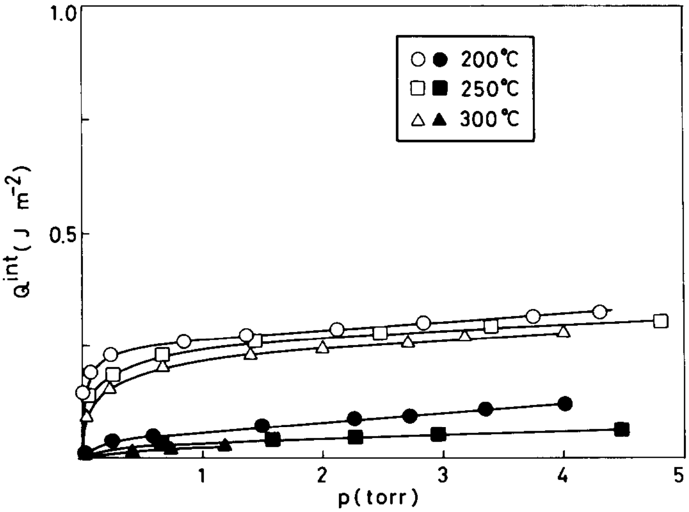

Fig. 1. Calorimetric isotherms: ○, □, △, run 1; ●, ■, ▲, run 2.

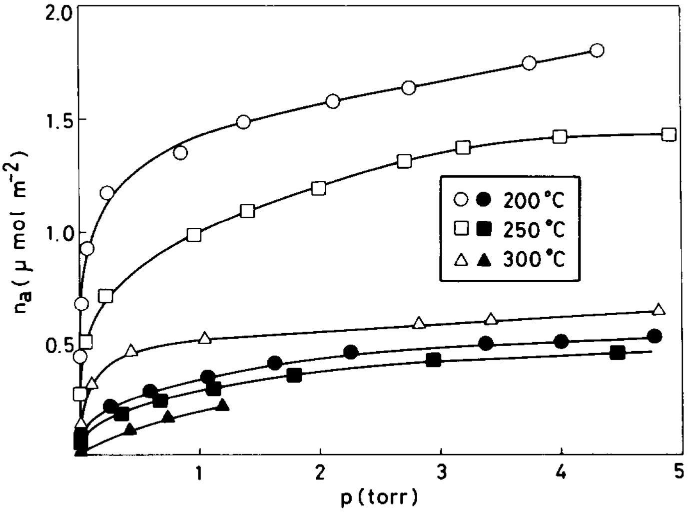

Fig. 2. Volumetric isotherms: ○, □, △, run 1; ●, ■, ▲, run 2.

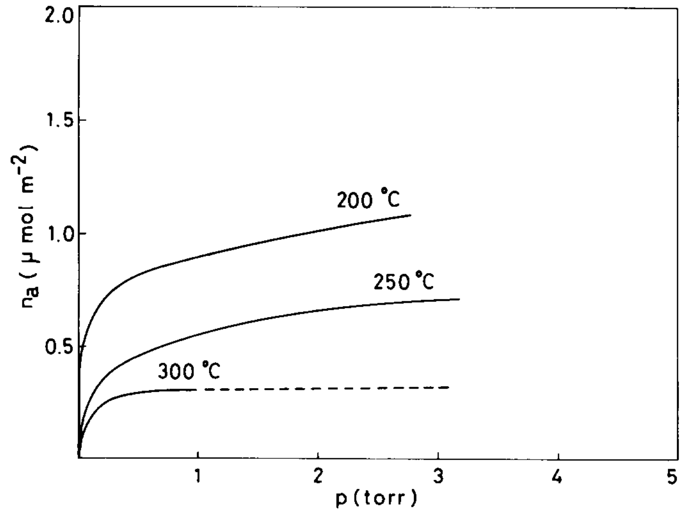

Fig. 3. Irreversible chemisorption at the three experimental temperatures (run 2 subtracted from run 1).

The volumetric isotherms of run 1 seem entirely Langmuiran in character (with completion of the monolayer at an equilibrium pressure of about 5 torr), and none of the isotherms has B.E.T. type-II behaviour, as observed for physisorption of H_2O, SO_2 and N_2 on high-energy surfaces. Figure 3 shows the amount of irreversibly adsorbed methanol at the three experimental temperatures.

It is very interesting to note that some of the methanol irreversibly bonded at 200°C becomes reversible at higher temperatures. The initial adsorption decreases with increasing temperature. Also the total amounts of irreversibly adsorbed methanol at each temperature (run 1 − run 2) decreases from 200 to 300°C.

Such data confirm the complexity of the process of chemisorption of methanol vapour on α-Al_2O_3 at high temperatures. In particular, we think that in the range 200–300°C, the simultaneous existence of different adsorption mechanisms is apparent. In fact when the sample of α-Al_2O_3 is degassed under vacuum at different temperatures, the surface hydroxyls react among themselves and form oxygen bridges and water, according to Exhibit 1 [6]

In contact with methanol vapour, the oxygen bridges react to form the

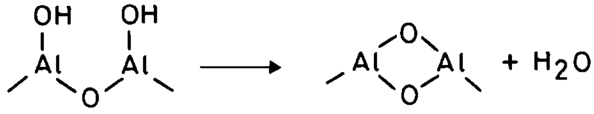

Exhibit 1.

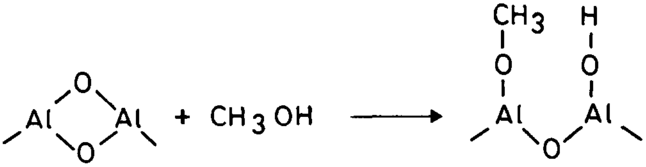

Exhibit 2.

methoxy species and new surface -OH groups (dissociative chemisorption), according to Exhibit 2.

The coordinative chemisorption of methanol vapour onto unsaturated aluminium ions is presented in Exhibit 3.

Such adsorption mechanism lead to irreversible and reversible phases, the balance of which depends on both coverage and temperature. We believe that irreversible chemisorption is present at very low coverage, according to the dissociative mechanism of methanol adsorption, and, at relatively higher coverage, reversible chemisorption is prevalent according to the coordinative mechanism of methanol adsorption on Al ions sites probably having tetrahedral or quasi-tetrahedral coordination [7]. The equilibrium between the two chemisorbed species is displaced towards the coordinative mechanism of adsorption with temperature increase.

Figure 4 shows the integral heats of chemisorption as a function of n_a (μmol m^{-2}), the adsorbed methanol vapour, for run 1. From these values, we can derive the differential heats of chemisorption as a function of n_a (μmol m^{-2}) of methanol vapour, for run 1 (Fig. 5). In this figure, the values of the differential heats of chemisorption at very low coverages for the three experimental temperatures (run 1) ($q_{\text{diff}} > 200$ kJ mol^{-1}) are higher than the respective values for the differential heats of run 2; in Fig. 5, the insert shows the differential heats of chemisorption for the reversible phases of adsorbed methanol. The first differential heats (run 1) (Fig. 5) appear to be independent of the experimental adsorption temperatures. If we make a comparison between these initial differential heats (271 kJ mol^{-1} at 200°C, 294 kJ mol^{-1} at 250°C and 262 kJ mol^{-1} at 300°C) and those obtained by adsorption of NH_3 on γ-Al_2O_3 (>200 kJ mol^{-1} at 150°C [8] and those obtained by adsorption of pyridine on Al_2O_3/SiO_2 (219 kJ mol^{-1} at 150°C

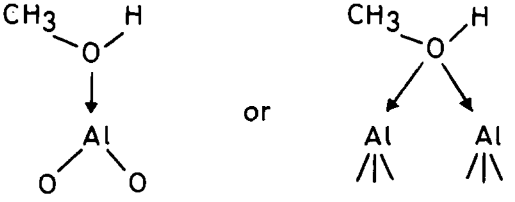

Exhibit 3.

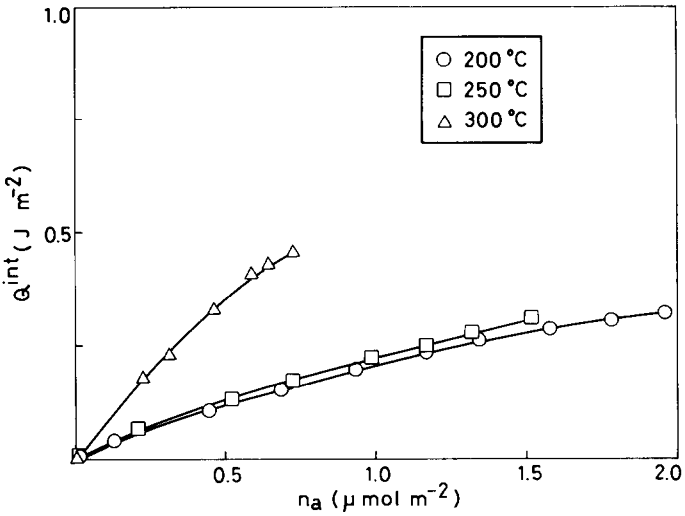

Fig. 4. Integral heats of chemisorption (run 1).

and 214 kJ mol^{-1} at 200°C [9]), we can conclude that these initial differential values could indicate strong Lewis-acid sites. In addition, the high differential heats of run 1 at very low coverage seem to confirm that the adsorption mechanism, in this case, is a dissociative irreversible chemisorption.

As shown in the insert of Fig. 5, the strong active sites available for

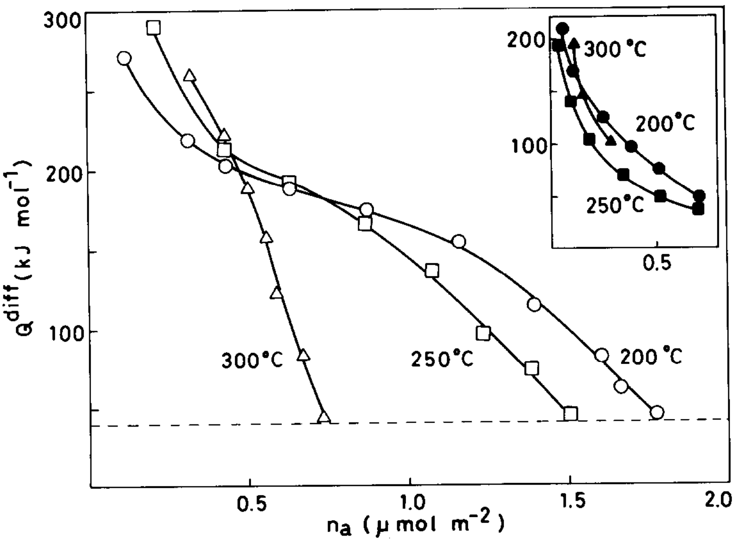

Fig. 5. Differential heats of chemisorption (run 1). In the insert, differential heats of chemisorption (run 2).

adsorption, at coverage below $n_a = 0.5\ \mu\text{mol m}^{-2}$, are not restored after desorption of α-Al_2O_3 for 4 h at 200, 250 and 300°C (always at 10^{-5} torr) in the cell inside the microcalorimeter.

The trend of differential heat values at the experimental temperatures 200 and 250°C are almost similar (Fig. 5). These curves show a decrease in the chemisorption heats with increasing coverage and may be interpreted as an indication of the successive formation of different adsorbed species of methanol vapour.

In particular, from the features of the curves, we note: (a) an initial region ($q_{\text{diff}} > 200\ \text{kJ mol}^{-1}$), probably representing chemisorption on the strongest sites; (b) a region of gradually decreasing heats, representing chemisorption on intermediate sites; (c) a region of low differential heats of adsorption (near $39\ \text{kJ mol}^{-1}$, the heat of methanol evaporation, as shown as a dashed line in the figure) [10] corresponding to H-bonded methanol.

The trend of the differential heat of methanol adsorption at 300°C (run 1, Fig. 5) is very interesting. The values fall abruptly from a high differential heat ($262\ \text{kJ mol}^{-1}$) to about $39\ \text{kJ mol}^{-1}$. A sudden decrease in the distribution of active sites probably occurs because, at high temperature, the formation of methoxy groups is delayed by the stabilization of the surface alumina structure [11]. The trend of the differential heats of the adsorbed methoxy groups, exchanged in a reversible way at 200, 250 and 300°C, is shown in the insert of Fig. 5. The surfaces appear less reactive and the values of the differential heats fall abruptly from about $200\ \text{kJ mol}^{-1}$ to $39\ \text{kJ mol}^{-1}$ for the temperatures 200 and 250°C. The less active sites seem to react by means of a coordinative mechanism. At 300°C, the sample of α-Al_2O_3 also seems less reactive than the same oxide surfaces at 200 and 250°C.

Finally we did not carry out the adsorption of methanol on α-Al_2O_3 at 350°C after the same conditions of pre-treatment of the sample (500°C and 10^{-5} torr for 5 h): the methanol is not adsorbed on the alumina surface, probably owing to strong stabilization of the surface structure of the oxide under investigation [11].

CONCLUSIONS

Adsorption microcalorimetry is a very useful technique for the study of solid–gas interactions at high temperature. We have shown that calorimetric measurements of the differential heats of methanol adsorption at 200, 250 and 300°C can be used to probe the distribution of active surface sites. Two phases of irreversibly and reversibly chemisorbed methoxy groups can exist on the surface of α-Al_2O_3. The amount of irreversible phase decreases as the experimental adsorption temperature increases.

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