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CHARACTERIZATION OF THE INTERACTION OF CO AND H_2 AT THE ZnO SURFACE BY ADSORPTION MICROCALORIMETRY

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CO and H_2 are both chemisorbed by ZnO but H_2 is more sensitive than CO to the surroundings of adsorption sites. When the two gases are coadsorbed, a strong interaction occurs, ascribed to the formation of a possible precursor in methanol synthesis.

CO и H_2 оба хемисорбируются на ZnO, но H_2 является более чувствительным к окружению на адсорбционных центрах, чем CO. Если оба газа соадсорбируются, то происходит сильное взаимодействие, приводящее к образованию возможного исходного продукта в синтезе метанола.

INTRODUCTION

The interaction between CO and H_2 on ZnO, leading to methanol synthesis in appropriate conditions has not yet been fully understood. A sort of intermediate surface complex is known to occur upon adsorption of the two gases, even at room temperature /1–3/ but its stoichiometry and stability are still debated. The adsorption of the two individual gases has been studied by many authors with various techniques /4–11/ but energy data are almost absent in the literature.

The present paper reports some preliminary results obtained by monitoring, by microcalorimetry, the adsorption of CO and H_2, and their interaction on ZnO.

Adsorption and related heats have been measured at room temperature with a Tian-Calvet microcalorimeter, connected to a volumetric apparatus /12, 13/, by introducing successive doses of the gas. Interaction between CO and H_2 was studied by adsorption of CO on variously H_2-covered ZnO.

Zinc oxide (Kadox 25) was pretreated in the calorimetric cell, following the procedure of other authors (outgassing and O_2 treatment at 400 °C, cooled in O_2 /7, 11/).

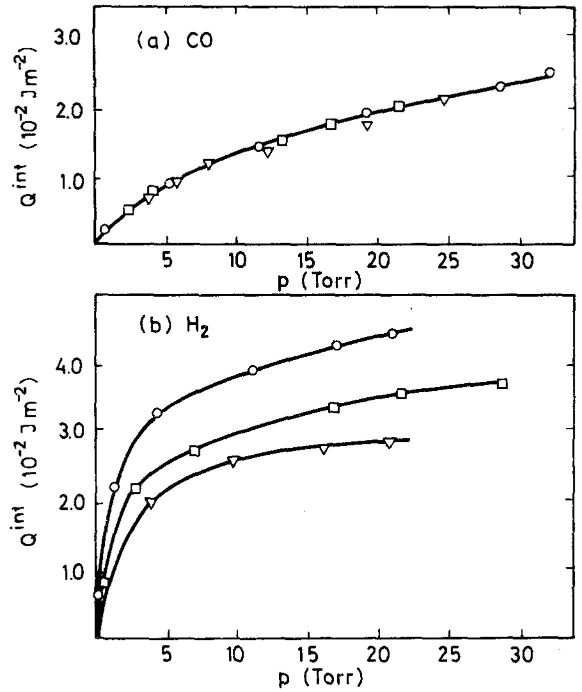

Fig. 1. Calorimetric isotherms: CO (1a) and H_2 (1b) adsorption on various ZnO samples

RESULTS AND DISCUSSION

a) *Variability in surface activity towards H_2 and CO chemisorption*

Adsorption of CO and H_2 on various samples is reported in Figs. 1a and 1b as calorimetric isotherms, i.e. evolved heats vs. equilibrium pressure; volumetric isotherms exhibit a similar shape.

The reproducibility of CO data is good (points from various measurements lie on the same curve) whereas hydrogen isotherms on each single sample differ from one another. The curves have all the same shape but the overall adsorptive capacity varies.

In contrast, the site distribution seems to be the same in all cases, as shown in Fig. 2, where the molar heat of adsorption of H_2 (Q^{int}/n_a) is plotted vs. equilibrium pressure (Fig. 2a) and the number of adsorbed moles (Fig. 2b). The energy of adsorption varies from an initial value of 60 kJ/mol to about 38 kJ/mol for all samples. All points lie on the same curve if plotted as a function of pressure but

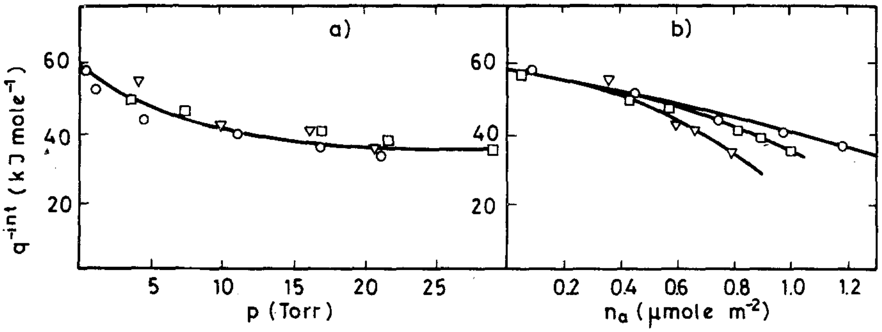

Fig. 2. Adsorption of H_2 on various ZnO samples: molar heat vs. pressure (a) and coverage (b)

Table 1

	Q_a^{int} (10^{-2} J m^{-2})	Q_d^{int} (10^{-2} J m^{-2})	% Q_{IRR}^{int}	t_0 (h)
a	1.17	1.10	5.9	0.5
b	1.15	1.07	6.9	0.5
c	4.31 3.85	2.45 2.47	43 36	18 17.5

follow different curves if plotted vs. adsorbed amounts. The variability from one sample to the other has therefore to be ascribed to a different adsorptive capacity towards H_2, not shown in the case of CO.

Slight occasional variation in thermal oxidizing treatments seem therefore to affect the adsorption of H_2 leaving that of CO basically unaffected. Taking into account that the reversible adsorption of CO and H_2 occurs on the same sites /11/; H_2 dissociation could be affected by small differences in the neighborhood of the active sites such as residual hydroxyls or adsorbed oxygen species, not affecting the coordination of CO by the unsaturated surface Zn^{2+}

b) *CO-H_2 interaction*

Evidence for interaction between CO and H_2 on ZnO surface, has been observed even at room temperature by several authors /1–3/. To investigate this point, the same dose of CO was admitted to: a) bare ZnO surface; b) ZnO precovered by H_2 adsorption and evacuated at room temperature; c) ZnO precovered by H_2 in equilibrium with a H_2 pressure of 10 Torr. Results are reported in Table 1, where

Q_a^{int} and Q_d^{int} are, respectively, the net heat of adsorption and desorption, % Q_{IRR}^{int} represents the fraction of heat related to irreversible processes and t_o is the duration of heat evolution.

A strong interaction occurs between CO and H_2 in case (c). No detectable differences in activity towards CO can be observed in cases (a) and (b). This confirms that the interaction occurs between CO and the reversible form of adsorbed H_2. Moreover, H_2 irreversibly bonded has no effect on this reaction. Three points can be singled out in the results obtained in case (c).

– The interaction of CO with H_2 at room temperature is slow and activated, whereas CO adsorption in cases (a) and (b) is an instantaneous process (Table 1, t_o).

– A remarkable increase in the heat evolved upon CO adsorption is observed (Table 1, column 1) in the presence of H_2 adsorbed reversibly; accordingly, the amount of adsorbate increases.

– Substantial amounts of products not removable from the surface are formed. Their extent is far larger than expected for adsorption of CO (0.07×10^{-2} J m^{-2} on the bare surface.

The present data clearly indicate that, even at room temperature, CO and H_2 react on ZnO to form surface species regarded as possible intermediate in methanol synthesis.

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