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Determination of the surface states of metallic clusters supported on alumina using microcalorimetry of CO adsorption

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Abstract

The adsorption of CO on alumina supported metal (Rh, Ru, Pt and Pd) catalysts was studied by microcalorimetry and infrared spectroscopy. The correlation of the results obtained from these two techniques provides information about the CO adsorbed species and the variations in the site energy distribution. Using these methods the nature and number of the surface sites on metal clusters, including aspects such as the presence of edge, corner or step atoms or the type of exposed crystalline planes, can be determined. Furthermore, the energetic distribution of surface sites has been shown to depend on the metal loading. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Supported metal catalysts; Alumina; CO adsorption; IR; Microcalorimetry

1. Introduction

In general, catalytic performance of metal catalysts depends on the metal particle size (structure sensitive reaction) and on the support employed [1,2]. Thus, to better understand the catalytic performance of metal catalysts a study of their surface chemistry seems to be necessary. Among many techniques available, adsorption microcalorimetry and infrared spectroscopy are very powerful tools. The former can provide information on the energy of interaction of reactive molecules with the surface of the catalyst, which is a parameter related with its surface structure [3,4]. While the latter, combined with adsorption of probe molecules, e.g. CO, can give useful information about the adsorption form of the probe molecule, and the surface chemical state and active sites of the catalyst. In this paper, we will present a comparative study by microcalorimetry of different metals (Ru, Rh, Pd and Pt) supported on alumina. We will carry out a surface analysis of supported Rh and Pd catalysts using infrared spectroscopy and adsorption calorimetry of the probe CO.

2. Experimental

2.1. Catalyst preparation

Al_2O_3 (Condea) with specific surface of 220 m^2/g was used as support. This material was calcined in air at 973 K for 4 h prior to metal loading. The supported ruthenium, rhodium and platinum catalysts containing 1 and 3 wt.% of the metal were prepared by incipient impregnation of the support with aqueous solutions of $Ru(NO)(NO_3)_3$, $RhCl_3{\cdot}xH_2O$ and $Pt(NH_3)_4Cl_2$, respectively. Palladium catalysts containing 1 and 3 wt.% of the metal were prepared by incipient impregnation of the support with aqueous solutions of $Pd(NO_3)_2$ and $Pd(NO_2)_2(NH_3)_2$, respectively. After

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drying, the catalyst precursors were calcined in air at 773 K for 2 h.

2.2. FTIR adsorption experiments

The calcined samples with Pd and Rh were pressed into self-supported wafers, ca. 10 mg/cm^2. A quartz IR cell with CaF_2 windows was used for the IR experiments. The temperature was increased at 10 K/min up to 673 K in a H_2 pulse (10^{-5} mol) and held at that temperature for 2 h. Subsequently, the catalyst was outgassed at 673 K for 1 h. The IR spectra of reduced samples were recorded before and after exposure to CO at room temperature. All the spectra were collected at room temperature on a Fourier transform infrared spectrometer (Nicolet 5 ZDX) equipped with a liquid nitrogen cooled mercury–cadmium–telluride (MCT) detector at a resolution of 4 cm^{-1} in the region 4000–1000 cm^{-1}. The results given herein are difference spectra with the spectrum of the clean sample before adsorption as the background.

2.3. Microcalorimetry measurements

The dispersion of metals was determined volumetrically by means of CO and H_2 adsorption, with simultaneous measure of the evolved heats by a Tian Calvet heat-flow calorimeter (Setaram C-80 II) operated isothermally at 330 K and connected to a glass vacuum adsorption apparatus. Doses of approximately 2×10^{17} molecules of the probe were introduced into the system to titrate the surface of metal catalysts. Both the calorimetric and volumetric data were stored and analysed by microcomputer processing. The apparatus has been described in detail elsewhere [5]. For experiments, the catalysts were first in situ reduced under hydrogen flow at 673 K for 2 h, outgassed overnight at the same temperature, and cooled to 330 K. The metal dispersion was obtained from the total amount of H_2 and CO uptake at the monolayer. This latter is considered to be covered when the evolved heat falls in the physisorption field (40 kJ/mol).

3. Results and discussion

Table 1 lists the metal dispersions of the different alumina supported catalysts. The metal dispersions were calculated by assuming a $M/H_2 = 2$ and $M/CO = 1$ stoichiometry. For Ru and Pt catalysts the dispersions obtained from H_2 and CO adsorption are in good accordance. This fact reveals that the CO molecules interact mainly with a surface ruthenium or platinum atom in a linear mode.

Table 1

H_2 and CO adsorption amount and metal dispersion of alumina supported metallic catalysts

Sample	N_{ads}-H_2 (μmol/g_{cat})	D (%)-H_2	N_{ads}-CO (μmol/g_{cat})	D (%)-CO
1% Rh/Al_2O_3	22	45.3	70	72.0
3% Rh/Al_2O_3	60	41.2	250	85.7
1% Pt/Al_2O_3	7	27.3	14	27.3
3% Pt/Al_2O_3	35	45.5	60	39.0
1% Ru/Al_2O_3	5	10.1	9.5	9.6
3% Ru/Al_2O_3	12.5	8.4	24	8.1
1% Pd/Al_2O_3	–	–	19	20.2
3% Pd/Al_2O_3	–	–	85	30.1

Figs. 1 and 2 show the differential heats of CO adsorption (ΔQ_{ads}) at 330 K as a function of surface coverage for Ru/Al_2O_3 and Pt/Al_2O_3 catalysts, respectively. The carbon monoxide coverage (θ) is

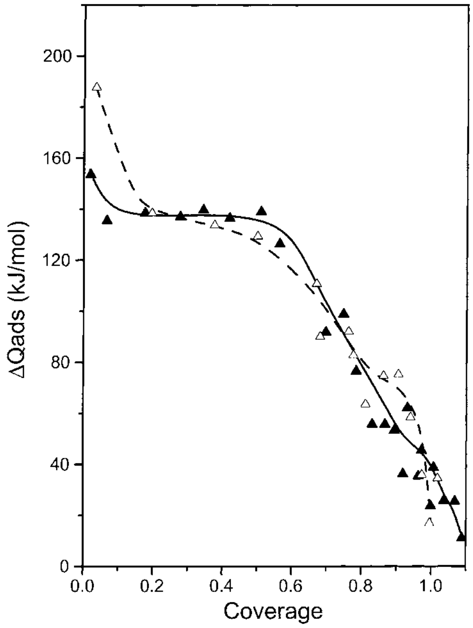

Fig. 1. Differential heats of CO adsorption at 330 K as a function of surface coverage for Ru/Al_2O_3: (▲) 1 wt.% Ru and (△) 3 wt.% Ru.

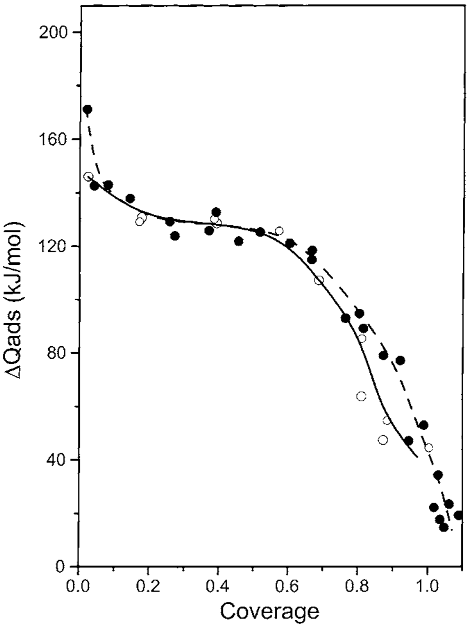

Fig. 2. Differential heats of CO adsorption at 330 K as a function of surface coverage for Pt/Al_2O_3: (●) 1 wt.% Pt and (○) 3 wt.% Pt.

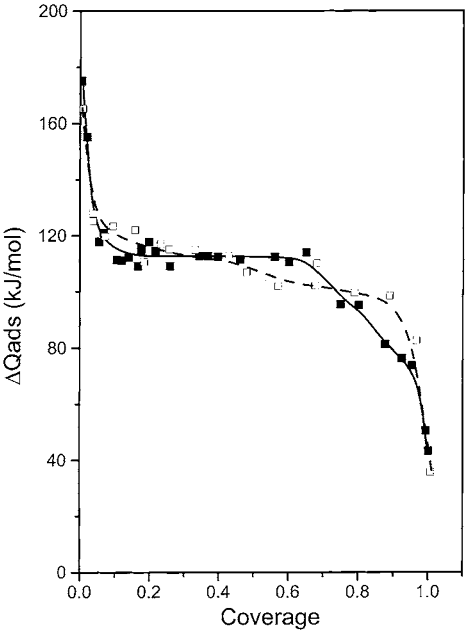

Fig. 3. Differential heats of CO adsorption at 330 K as a function of surface coverage for Rh/Al_2O_3: (■) 1 wt.% Rh and (□) 3 wt.% Rh.

determined as the ratio between the adsorbed amount at a given point and the monolayer uptake of the sample. This procedure facilitates comparison of catalysts with different metal loading and dispersions. Observation of the curves reveals one plateau at 140 kJ/mol in 1 and 3 wt.% Ru samples and at 130 kJ/mol in 1 and 3 wt.% Pt samples. Similar values for heats of CO adsorption on single crystal surfaces of Pt and Ru have been reported [6]. It is noteworthy that the constant value of the plateau extends over a wider range of surface coverage for samples with the lower loading, 1 wt.% metal. This finding indicates a higher homogeneity of the surface metal atoms of the 1% Pt/Al_2O_3 and 1% Ru/Al_2O_3 samples for the CO adsorption. The higher initial heat of adsorption obtained in the samples can be attributed to the interaction of CO with highly unsaturated metal atoms at corners and edges.

As Rh catalysts concerned, metal dispersions obtained from CO adsorption are higher than that obtained from H_2 adsorption. It can be inferred that one rhodium atom adsorbs more than one CO molecule. Fig. 3 gives the differential CO adsorption heat versus coverage profiles of the Rh/Al_2O_3 catalysts. It can be seen that 1% Rh/Al_2O_3 sample exhibits an initial differential heat of CO adsorption of ~170 kJ/mol. The initial adsorption heat decreases to a large plateau at ca. 110 kJ/mol, in the region of $\theta = 0.05$–0.6. The quite constant value over a wide range indicates a homogeneous CO adsorption behaviour of the 1% Rh/Al_2O_3 sample. Fig. 4 shows the IR spectra of CO adsorbed on 1 and 3% Rh/Al_2O_3. Two IR bands are observed at 2099 and 2030 cm^{-1} indicating the formation of *gem*-dicarbonyl CO species [7]. These bands are overlapped with the IR band of the linear species (2068 cm^{-1}). In addition, a broad IR band is detected at ~1850 cm^{-1} due to a bridged CO species [7]. The high initial adsorption heat evolved can be attributed to the formation of the bridged CO species detected. Moreover, the high population of sites with similar adsorption heat, 110 kJ/mol, agrees with the formation mainly of one well-differentiated dicarbonyl species revealed by infrared studies (Fig. 4). However, the calorimetric profile of the 3% Rh/Al_2O_3 sample does not show a plateau with a very constant value. But a slow and continuous decline from 120 to 100 kJ/mol in the wide region of $\theta = 0.1$–0.9 is observed, before a drastic fall of the evolved heat to the physisorption field. This fact

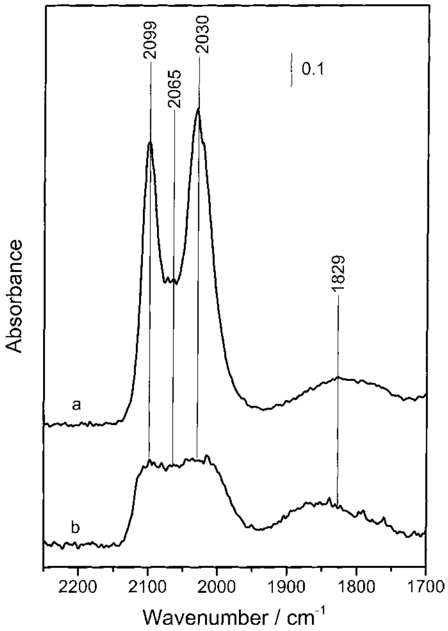

Fig. 4. IR spectra of CO adsorbed on Rh/Al_2O_3 with different metal loading: (a) 1 wt.% Rh and (b) 3 wt.% Rh.

reveals a relatively heterogeneous surface sites energy distribution for the sample with higher metal loading. The infrared spectrum (Fig. 4b) shows a broad band at ca. 2120–2000 cm^{-1} which can be assigned to different dicarbonyl species and linear-bonded CO. Since dicarbonyls are formed on well-dispersed rhodium, and linear and bridge CO species on crystalline rhodium, a growing number of larger clusters can be inferred when the metal content is increased. The IR results confirm the existence of various dicarbonyl species slightly different from the energetic point of view.

We have recently studied the interaction of Pd with different supports by microcalorimetry and infrared spectroscopy of CO adsorption [8,9]. We found that the support material influences the fraction of Pd sites adsorbing the CO in a specific mode. Fig. 5 gives the differential adsorption heat versus CO coverage and Fig. 6 displays the IR spectra of CO on 1 and 3% Pd/ Al_2O_3 catalysts. The microcalorimetry results of CO adsorbed on Pd/Al_2O_3 reveals that three zones with characteristic values at the high (200 kJ/mol), medium (140–120 kJ/mol), and low (100–80 kJ/mol) regions of adsorption differential heat. However, the energetic

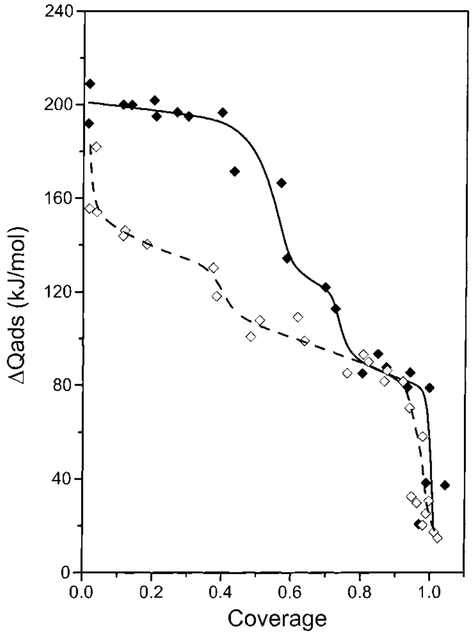

Fig. 5. Differential heats of CO adsorption at 330 K as a function of surface coverage for Pd/Al_2O_3: (◆) 1 wt.% Pd and (◇) 3 wt.% Pd.

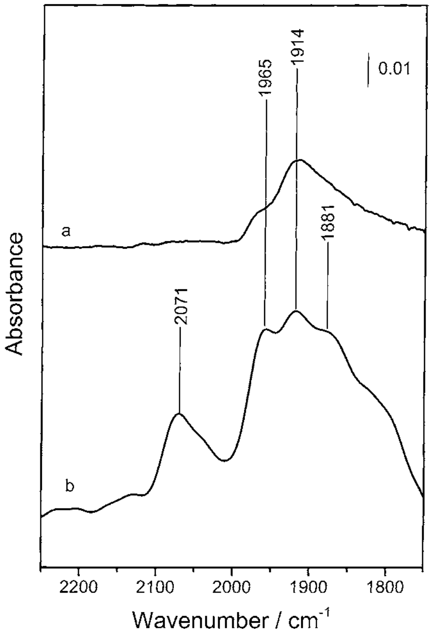

Fig. 6. IR spectra of CO adsorbed on Pd/Al_2O_3 with different metal loading: (a) 1 wt.% Pd and (b) 3 wt.% Pd.

distribution of surface CO adsorption sites is a function of the metal loading.

The IR spectra show three bands at 2071, 1965 and 1914, which can be attributed to linearly adsorbed CO, and bridge-bonded CO on Pd(1 0 0) and Pd(1 1 1) planes, respectively [10–12]. Besides these another band at ca. 1880 cm^{-1} due to multibonded CO species exists, overlapped with the 1914 cm^{-1} band. It is noteworthy that the intensities of the bands due to linear CO species (2071 cm^{-1}) and bridged CO on Pd(1 0 0) plane increase with the metal loading, while that corresponding to multibonded CO species diminishes.

Based on the IR results the three regions (high, medium and low) of adsorption heat showed by the calorimetric curves can be attributed to the formation of multibonded, bridged and linear CO species adsorbed on palladium, respectively. Thus, the depletion in the surface population of multibonded CO species and the enhancement of the linear and bridged CO species caused by the increase in the palladium loading, as seen in the IR spectra, are consistent with the narrowing of the plateau at high adsorption heat (200 kJ/mol) and the enlargement of those corresponding to medium (140–120 kJ/mol) and low (80–100 kJ/mol) adsorption heats.

The previous results have permitted a classification in number, strength and energy distribution of the surface CO adsorption sites of alumina-supported platinum, ruthenium, rhodium and palladium catalysts. So, complex calorimetric curves presenting two or three populations of surface sites of different adsorption strength have been correlated to the different forms of adsorption encountered at the surface by IR. It can be concluded that the fraction of surface sites adsorbing CO in a specific mode is a function of the nature and loading of the metal catalyst.

Acknowledgements

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