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Surface sites on carbon-supported Ru, Co and Ni nanoparticles as determined by microcalorimetry of CO adsorption

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Abstract

The adsorption of CO on carbon-supported metal (Ru, Co and Ni) catalysts was studied by microcalorimetry. A correlation of the results thus obtained with those reported for monocrystals or with other studies available in the scientific literature for supported metal catalysts, including infrared spectroscopy data, enables the determination of the type of exposed crystalline planes and/or of the different types of CO adsorbed species. The results obtained suggest that the energetic distribution of the surface sites depends on the carbon support material and on the applied reduction treatment. In this way, the use of a high surface area graphite (clean of surface oxygen groups) leads to an electron density enrichment on the small metal particles (Ru) and, in general, to a higher heterogeneity of the active surface sites. The elimination of surface oxygen functional groups (with the reduction treatment at the higher temperature) of the carbon molecular sieve support leads to changes in the surface structure of the metal particles and, consequently, to higher CO adsorption heats, particularly for Ru and Co.

Keywords: Supported metal catalysts; Carbon supports; CO adsorption; Microcalorimetry

1. Introduction

Carbon-supported metal catalysts are widely used, for instance, for the production of *fine chemicals*, where the surface structure of the metallic nanoparticles is crucial, for example, for the production of the desired stereoisomer [1]. Thus, to better understand the catalytic performance of these catalysts a study of their surface chemistry seems to be necessary. Unfortunately, the surface structure of carbon-supported catalysts cannot be characterized by the so commonly used spectroscopic techniques (e.g. Fourier-transformed infrared spectroscopy (FT-IR)). So, among the techniques available, adsorption microcalorimetry seems to be a very convenient tool, since it can provide information concerning the energy of interaction of probe molecules with the surface of the catalyst, which is a parameter related with its surface structure [2,3]. In this paper we will present a comparative study of different metals (Ru, Co and Ni) supported on two different carbon materials by means of CO adsorption microcalorimetry. We will emphasise on the effect of the carbon supports with different porous structure and crystallinity, and of the pretreatment conditions, which originate modifications on the surface structure of the metal particles. Also, some speculative discussions about the surface reorganization, based on the comparison of adsorption heats determined on monocrystals, or about the different types of adsorbed CO species formed on the metallic surface sites of metal nanoparticles is presented.

2. Experimental

2.1. Catalyst preparation

Two carbon materials were used as supports. The first one is a mesoporous high surface area graphite (H; $S_{BET} = 297\ m^2/g$) prepared by treatment under a N_2 continuous flow

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at 1173 K of commercial HSAG-300 (Lonza Ltd.). This treatment provides a clean carbon surface, free of oxygen functional groups, with textural and structural properties similar to those of the starting commercial material [4]. The second one is a microporous carbon molecular sieve (S; $S_{BET} = 1500\ m^2/g$) that was prepared as follows. Copolymer Saran (90% vinylidene chloride–10% vinyl chloride, Aldrich) was carbonised in a N_2 continuous flow at 1073 K (2 h), and activated by 17 oxidation–decomposition cycles, that is, oxidation at 473 K (6 h) under a continuous flow of air, followed by decomposition in flowing N_2 at 1223 K (2 h). The activation process implies oxygen chemisorption at 473 K, and decomposition at 1223 K of the so generated surface oxygen functional groups. On the last activation cycle, only the oxidation treatment was performed to evaluate the presence of surface oxygen functional groups of the carboxylic acid, lactone, phenolic and carbonylic types, as determined by temperature-programmed desorption (TPD-MS) experiments [1].

Metal catalysts M*x*H and M*x*S (M = Ru, Co, Ni; *x* = wt.% metal loading) were prepared by the incipient wetness technique by impregnation of the carbon materials with the corresponding metal salt water solution ($Ru(NO)(NO_3)_3$, $Co(NO_3)_2\cdot 6H_2O$, $Ni(NO_3)_2\cdot 6H_2O$) in order to obtain samples with 2 wt.% Ru and 5 wt.% Co and Ni.

2.2. *CO adsorption microcalorimetry measurements*

The CO chemisorption isotherms were determined volumetrically and the evolved heats in each pulse were measured simultaneously by means of a Tian Calvet heat-flow calorimeter (Setaram C-80 II) operated isothermally at 330 K and connected to a glass vacuum-dosing apparatus. Pulses of ca. 2×10^{17} molecules of the probe gas were introduced into the system to titrate the surface of the metal catalysts. Both calorimetric and volumetric data were stored and analysed by microcomputer processing. The apparatus has been described in detail elsewhere [5]. Previous to adsorption experiments, the catalysts were in situ reduced under hydrogen flow at 673 or 773 K for 2 h, out-gassed overnight at the same temperature, and cooled to 330 K under vacuum. The metal dispersions (D) were calculated from the total CO uptake at the monolayer (N_{ads}), considered to be attained when the evolved heat falls to the physisorption field (ca. 40 kJ/mol), and assuming a M:CO = 1:1 stoichiometry [6,7]. The mean crystallite sizes were calculated from dispersion values, assuming spherical metal particles, using the equation d (nm) = υ/D ($\upsilon = 1.32$, 0.99 and 1.01 for Ru, Co and Ni, respectively) [8]. The microcalorimetric profiles that will be shown in the present work represent the variations in the differential CO adsorption heats with the carbon monoxide coverage (θ). The latest is determined as the ratio between the adsorbed amount at a given point and the monolayer uptake (N_{ads}) of the sample. This procedure facilitates comparison of catalysts with different dispersions.

3. Results and discussion

Table 1 shows the CO adsorption volumetric amount (N_{ads}; $\mu mol/g_{cat}$), dispersion (D; %) and mean particle size (d; nm) values determined from the CO chemisorption measurements for the different carbon-supported metal samples. Metal particles are larger (d) on the Co and Ni samples than on the Ru ones, independent of the reduction temperature and of the carbon support. When reduced at 773 K, in general, the catalysts suffer sintering of the metal particles but among them, Co5H experiences the most acute sintering. In general, it can also be observed that when the graphite material is used as support larger metal particles are obtained, independent of the applied reduction temperature and of the metal (this effect is much more acute, again, for Co). This could be explained as due to specific interactions between the surface oxygen functional groups of the Saran support and the metal salt precursors, which are absent in the case of the graphite material. The presence of such specific interactions would force a good dispersion of the precursor leading to the formation of smaller metal particles during the course of the reduction treatment.

Also, initial CO adsorption heats (q^0_{ads}) are shown to enable comparison among catalysts. This value is determined by extrapolation to zero coverage of the chemisorption heat curves thus obtained from the adsorption microcalorimetric experiments.

3.1. *CO adsorption microcalorimetric profiles of Ru catalysts*

Fig. 1 shows the CO differential heats versus coverage plots corresponding to the Ru catalysts for reduction treat-

Table 1
Surface properties of carbon-supported Ru, Co and Ni samples, reduced at 673 and 773 K as determined by CO chemisorption

Catalyst	M (%)	Reduced at 673 K				Reduced at 773 K			
		N_{ads} ($\mu mol/g_{cat}$)	D (%)	d (nm)	q^0_{ads} (kJ/mol)	N_{ads} ($\mu mol/g_{cat}$)	D (%)	d (nm)	q^0_{ads} (kJ/mol)
Ru2S	1.9	93	51	2.6	116	50	27	4.9	140
Ru2H	2.0	79	39	3.4	140	58	29	4.6	145
Co5S	4.8	125	15	6.4	140	44	5.4	18	117
Co5H	4.7	80	10	9.8	107	16	2.0	50	120
Ni5S	4.4	57	7.6	13	121	37	5.0	20	120
Ni5H	4.0	45	6.6	15	125	25	3.6	28	125

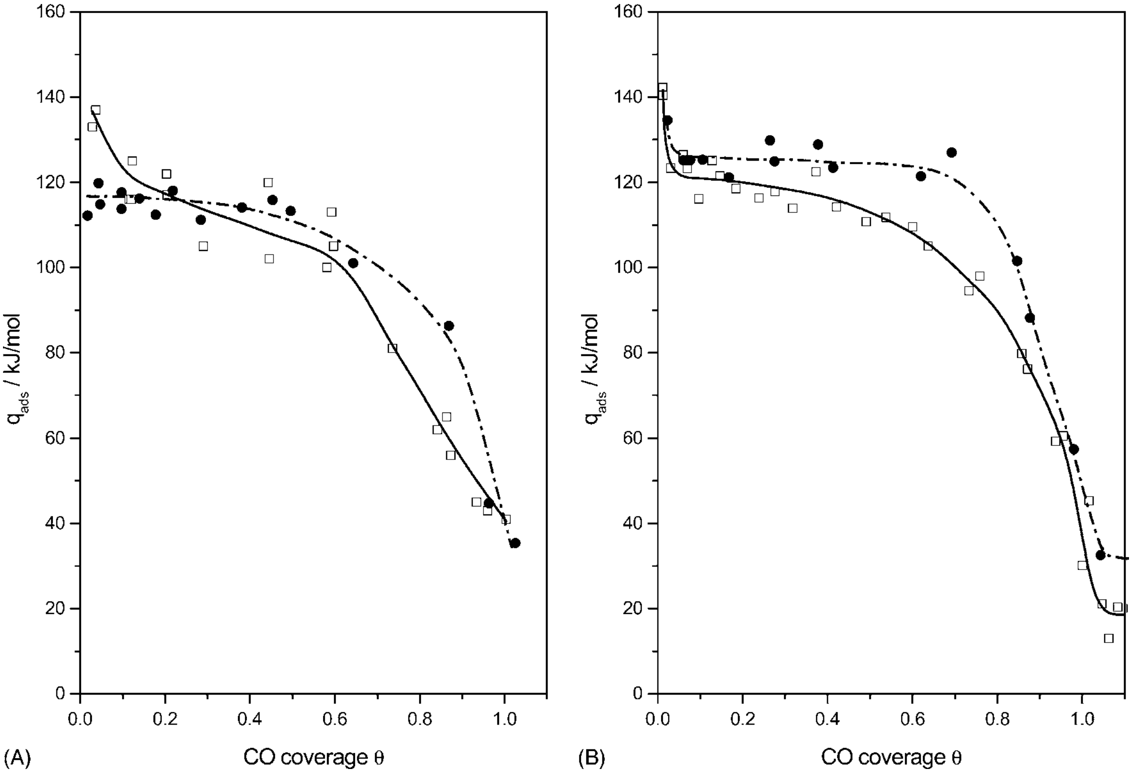

Fig. 1. Differential heats of CO adsorption at 330 K as a function of surface coverage for Ru2H (□) and Ru2S (●) reduced at 673 K (A), and reduced at 773 K (B).

ments at 673 and 773 K. For both treatments it may be observed that the surface site distribution is very different depending on the carbon support. When reduced at 673 K (Fig. 1A) a more homogeneous surface site distribution is observed for Ru2S, since a large *plateau* at ca. 116 kJ/mol from initial to medium CO coverages is shown. On the other hand, for Ru2H it is observed that a sharp fall of the initial adsorption heat is produced to reach a heat of 118 kJ/mol at ca. $\theta \sim 0.2$. Then a continuous but slow decay of the differential heats (from 115 to 105 kJ/mol) is observed until $\theta \sim 0.6$. Further increase in the CO coverage produces a sharp fall in the adsorption heat values until monolayer formation (ca. 40 kJ/mol). It is also important to point out the difference in the adsorption heats for the low coverage range between these two catalysts. Ru2S shows initial heat values of ca. 116 kJ/mol, while for Ru2H initial heat values are ca. 140 kJ/mol, in agreement with similar studies [9–11]. It has been postulated that in high surface area graphite-supported catalysts an electronic transfer from the support to the metal particles may be produced, and that this effect will be favoured when the metal particles are located at edges and corners of graphitic sheets that are clean of surface oxygen functional groups [4,10]. Such electronic transfer would make the contribution of the M–C π-bond higher and hence higher CO adsorption heats would be obtained. Also, the functional oxygen groups present at the surface of the Saran support could be responsible of the lower initial CO adsorption heats, since these groups could withdraw electron density from the smaller Ru particles.

Again, when reduced at 773 K (Fig. 1B) the profiles show some differences regarding the distribution and type of surface sites. Ru2H shows a more heterogeneous surface site distribution than Ru2S. Ru2H shows an initial adsorption heat of ca. 145 kJ/mol with a sharp fall to 120 kJ/mol at $\theta \sim 0.03$. From such coverage value heats gradually fall until ca. $\theta \sim 0.8$, to then sharply decrease until monolayer attainment (ca. 40 kJ/mol). These results contrast with those of Ru2S. For this latest sample the microcalorimetric profile starts with a CO initial adsorption heat of ca. 140 kJ/mol that sharply falls to reach a *plateau* at ca. 126 kJ/mol for the $\theta \sim 0.05$–0.65 range. Once a 0.65 coverage is attained, heats sharply fall to the physisorption field.

Different to what was found when the sample was reduced at 673 K, Ru2S shows high initial adsorption heat values similar to those of Ru2H. Also, this latest shows lower heat values almost for the entire θ range. Taking into account that no important differences on the surface site distribution or on the CO adsorption heat values are observed for Ru2H on increasing the reduction temperature, and that the metal particle sizes of Ru2H and Ru2S (reduced at 773 K) are very similar, the sharp increase in the adsorption heats of Ru2S when reduced at 773 K (compared to the same sample reduced at 673 K, Fig. 2) has to be due to something more than the simple increase of the electron density of the Ru sites due to the enlargement of the metal particles (Table 1). Changes in particle structure and/or morphology, and generation of different adsorption centres may be

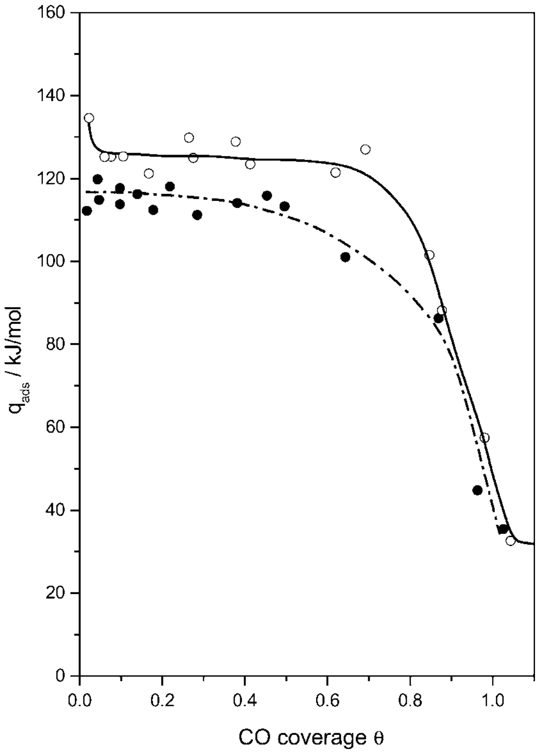

Fig. 2. Comparison of the microcalorimetric profiles of Ru2S reduced at 673 (●) and 773 K (○).

taking place when increasing the reduction temperature on this Ru2S sample. In fact, the elimination of surface oxygen functional groups of the Saran support, as determined by temperature-programmed reduction (TPR) and TPD-MS experiments [1], could be responsible, on the one hand, of metal sintering and, on the other hand, of a structure/morphology rearrangement of the metal particles, leading to such heat variations. The CO adsorption heat values that appear in the literature for Ru (1 0 0) are ca. 105–120 kJ/mol [12] and 124 kJ/mol [13], while a 160 kJ/mol [14] value is found for the (0 0 1) plane, and 105–120 kJ/mol for the (1 1 0) face arrangement [12]. These data seem to indicate that Ru particles in these Ru catalysts (both reduced at 673 and 773 K) expose mainly (1 0 0) and (1 1 0) planes. Even though we cannot rule out the possibility that the relative (1 0 0)/(1 1 0) plane ratios could be different depending on the carbon support.

Comparison of the current microcalorimetric results with FT-IR of adsorbed CO studies on SiO_2-supported Ru catalysts [15], enables us to suggest the presence of bridged (Ru_2CO) and linear (Ru–CO) CO species adsorbed on our supported Ru particles, corresponding to adsorption heat values of ca. 140 and 100–130 kJ/mol, respectively. A slight increase of the bridged CO species population over Ru sites may be taking place when increasing the reduction temperature of both Ru2H and Ru2S, in agreement with the increase in the mean metal particle size.

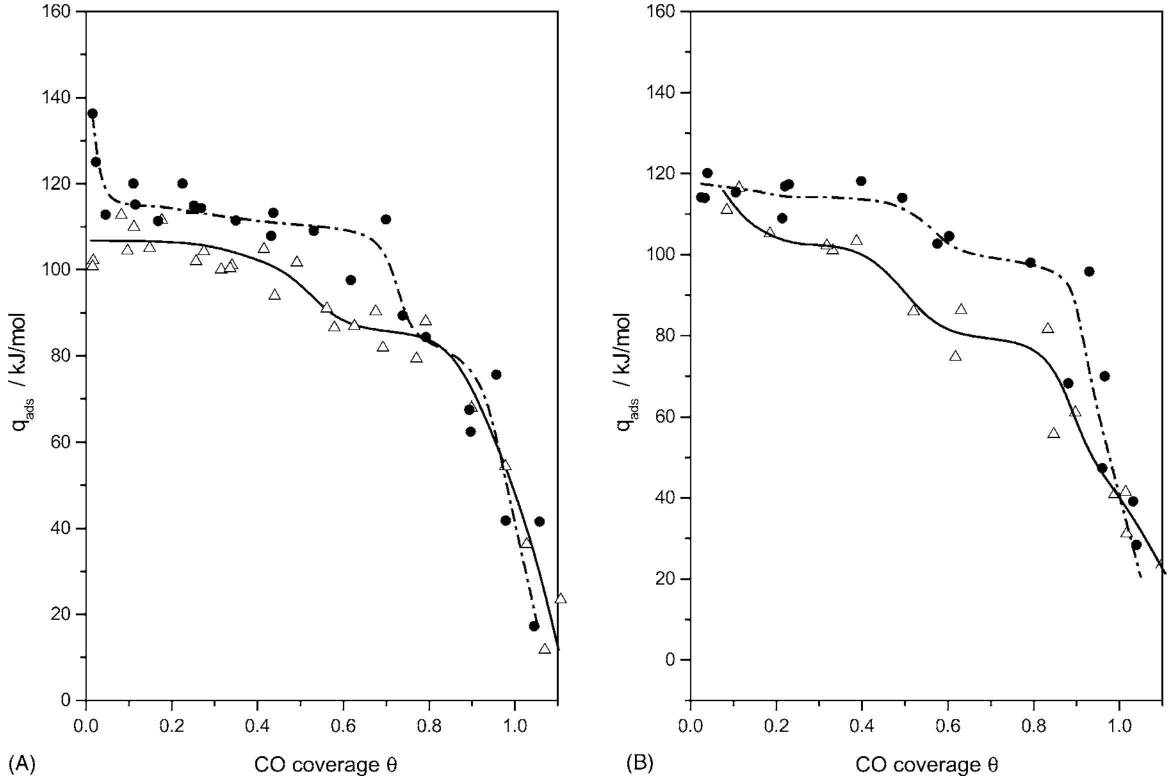

Fig. 3. Differential heats of CO adsorption at 330 K as a function of surface coverage for Co5H (△) and Co5S (●) reduced at 673 K (A), and reduced at 773 K (B).

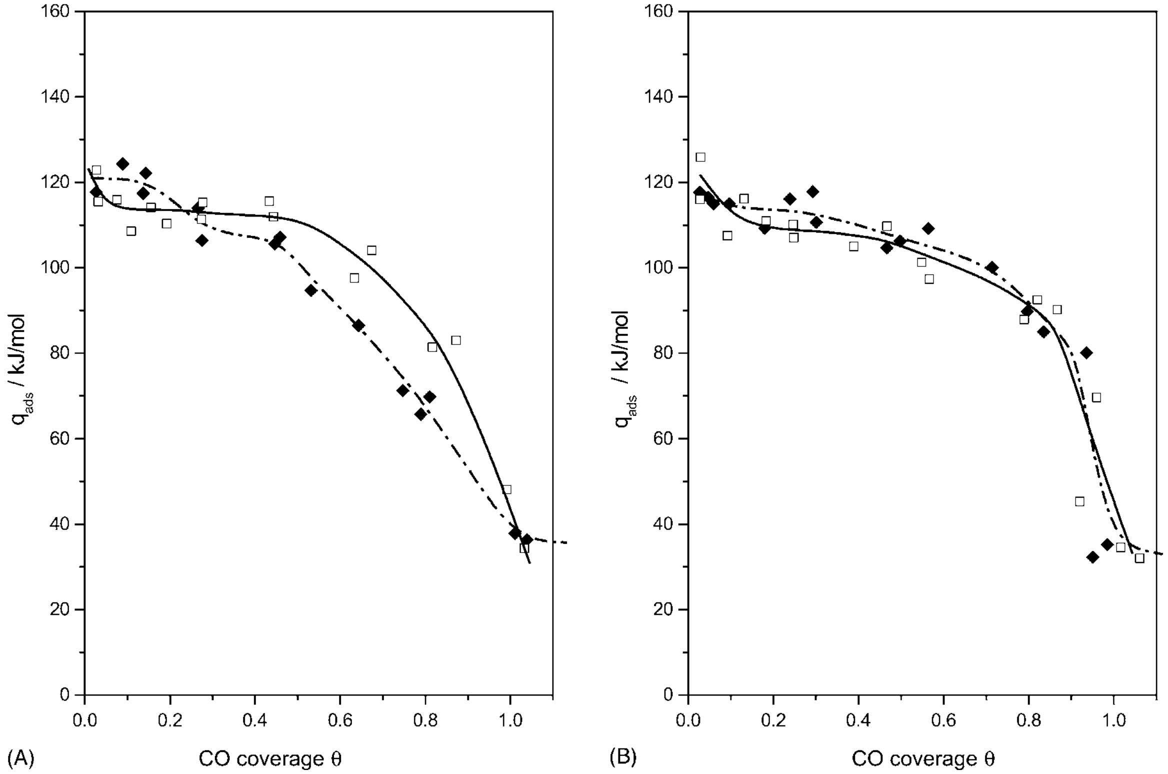

Fig. 4. Differential heats of CO adsorption at 330 K as a function of surface coverage for Ni5H (■) and Ni5S (□) reduced at 673 K (A), and reduced at 773 K (B).

3.2. CO adsorption microcalorimetric profiles of Co catalysts

Co catalysts reduced at 673 K (Fig. 3A) show very different microcalorimetric profiles, and not only for the low coverage region but for all the θ range where Co5S shows higher CO adsorption heats. This catalyst shows a high initial adsorption heat of ca. 140 kJ/mol. The population of sites with such a high CO (initial) adsorption heat is small, and a continuous and sharp decay of the differential heats is observed to reach a *plateau* at ca. 112 kJ/mol in the 0.1–0.7 coverage region. Then, heats fall again until a very narrow *plateau* is reached at ca. 85 kJ/mol in the 0.8–0.9 range, to finally fall to the physisorption field (ca. 40 kJ/mol). On the other hand, Co5H shows a microcalorimetric profile with two *plateaux* at ca. 107 (low to medium coverages) and 85 kJ/mol ($\theta \sim 0.6$–0.8). Further increase in the CO coverage produces a sharp fall in the adsorption heat values until monolayer attainment. The apparition of the two constant CO heat values for both Co catalysts is indicative of two homogeneous surface site distributions, and hence of the apparition of two different types of surface Co active sites for CO chemisorption. Comparison of these results with FT-IR of adsorbed CO studies over Co/SiO_2 [16,17] enables us to suggest the presence of linear Co^0–CO (100–120 kJ/mol) and policarbonylic $Co(CO)_x$ ($x > 1$) species (70–90 kJ/mol) adsorbed on our supported Co particles. For Co5S, considering the high adsorption heat values in the low coverage range, bridged CO species (Co_2CO) would also be present (ca. 130–140 kJ/mol). We may say that the differences in the CO adsorption heat values (among these Co catalysts) for the different adsorbed species may be related to differences in particle structure and/or morphology due to the support. That is, the energetic differences shown by the surface sites for linear and policarbonylic adsorption (corners, edges, and plane sites) could be due to the carbon material used as support. Also, we have to consider that for the same adsorption stoichiometry, it has been postulated that the most energetic sites are those located at corners and edges of the metal particles, the population of such sites being higher on smaller metal particles. Considering that metal particles in Co5S are smaller than in Co5H (Table 1), it is more probable to find a higher proportion of particle irregularities and hence stronger adsorption sites (corners and edges) on the metal particles of Co5S.

When reduced at 773 K (Fig. 3B) the microcalorimetric profiles of the Co catalysts show even more acute differences depending on the carbon support employed. The general profiles do not differ significantly from those of the same samples reduced at 673 K, but it may be observed that when reduced at 773 K the energetic differences between the two samples are higher (as for Co5H heat values decrease slightly and those of Co5S increase slightly respect to the same samples reduced at 673 K). Co5S shows two *plateaux* at ca. 117 ($\theta \sim 0.1$–0.5) and 106 kJ/mol ($\theta \sim 0.6$–0.85), while Co5H shows *plateaux* at ca. 105 ($\theta \sim 0.2$–0.4) and 80 kJ/mol ($\theta \sim 0.6$–0.8). Again, the apparition of two constant heat values indicates the formation of two different CO adsorbed species over the Co particles. For Co5H reduced at 773 K the CO adsorbed species would be the same as those for the same sample reduced at 673 K (linear and policarbonylic). However, it seems that two different linear Co^0–CO species are formed over the Co particles of Co5S. These results suggest that the morphology and or structure of the Co particles are somewhat different depending on the carbon material employed as support. As previously suggested for the RuS sample, a change in the surface structure of Co5S may be taking place when reduced at 773 K, due to the elimination of surface oxygen functional groups of the S support [1].

3.3. CO adsorption microcalorimetric profiles of Ni catalysts

The microcalorimetric profiles of the Ni catalysts reduced at 673 K (Fig. 4A) reveal only slight differences regarding the heterogeneity of the surface sites, that is higher for Ni5S. This catalyst shows an initial adsorption heat of ca. 121 kJ/mol with a *plateau* in the low coverage range. Then heat values decrease to another *plateau*, comprising the 0.3–0.45 coverage region at ca. 107 kJ/mol, to finally fall to the physisorption field. On the other hand, Ni5H shows an initial adsorption heat of ca. 125 kJ/mol that falls to reach a *plateau* in the 0.1–0.5 coverage range at ca. 113 kJ/mol. Finally, heats fall gently to reach the weak adsorption field. In general, no important surface site distribution differences are observed for these Ni catalysts.

When reduced at 773 K (Fig. 4B) even less differences are observed. The surface site distribution of Ni5H and Ni5S seems to be almost identical, suggesting that metal particle morphology, structure (type of crystallographic plane/s exposed), and adsorbed CO species are the same independent of the carbon material used as support. Both profiles show initial adsorption heats around 120 kJ/mol that fall to reach a *plateau* around 110 kJ/mol in the ca. 0.2–0.45 coverage range. Then heats gradually fall until a coverage of 0.85 to finally fall in a more sharp fashion until monolayer attainment.

It has to be pointed out that initial CO adsorption heat values obtained with our Ni catalysts fit well with those found in the literature for CO adsorption over sites on the Ni (1 0 0) plane [18–20]. Also, such heats may be ascribed to linearly adsorbed CO over metallic Ni (Ni^0–CO) as previously suggested for Ni powder [21], corresponding to the 100–130 kJ/mol heat region. Since these initial heat values decrease slightly on increasing the CO coverage, a small contribution of policarbonylic species ($Ni(CO)_x$; $x = 2$ or 3) could also be possible, as IR studies suggest for alumina and silica-supported Ni catalysts [22].

4. Conclusions

The following conclusions can be deduced from the former discussion:

- Ru2H catalyst shows a more heterogeneous distribution of differential adsorption heats with CO coverage respect to that of Ru2S.
- The use of H as support leads to an electron density enrichment of the smaller Ru particles (generated with a reduction treatment at 673 K), and the presence of surface oxygen functional groups (not completely removed with the reduction treatment at 673 K) at the surface of the Saran support produces electron deficient Ru particles.
- The removal of surface oxygen functional groups, present at the surface of the Saran support, with the reduction treatment at 773 K, produces an important increase of the CO initial adsorption heats over Ru2S.
- Co particles exhibit the most important changes on their surface structure and hence on the CO adsorption modes when the carbon support is changed. The distribution of surface active sites on the Ni catalysts (Ni5H and Ni5S), described by CO adsorption microcalorimetry, is independent of the reduction temperature and the support employed.

From the above conclusions we may say that microcalorimetry of CO adsorption is a valuable tool to determine the distribution of surface sites and adsorption modes on carbon-supported catalysts.

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